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ORGANIC PESTICIDES AND PESTICIDE CONTAINERS

A Study of Their Decontamination and Combustion

This report (SW-21c) was prepared for the
Federal solid waste management program by

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FOREWORD

A major emphasis of the 1965 Solid Waste Disposal Act and its amending 1970 legislation is directed toward rectifying inefficient and improper methods of disposal that create serious hazards to public health, including the pollution of air and water resources. In this respect, pesticide wastes are a growing concern. These difficult-to-dispose-of wastes are expected to receive more attention in the future, as has been evident in recent legislation.

The Office of Solid Waste Management Programs decided to investigate specific combustion temperatures and general burning characteristics of representative pesticides in order that a complete and safe method of decontamination and disposal could be recommended. This report represents the results of that investigation under contract to the Foster D. Snell, Inc., Florham Park, New Jersey. The Office of Solid Waste Management Programs was represented by Henry Johnson during the implementation of the contract and the preparation of the report.

--RICHARD D. VAUGHAN
Deputy Assistant Administrator
for Solid Waste Management

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SUMMARY

The purpose of this project was to investigate methods of combustion applicable to residues of pesticides and their containers and to devise a means for their destruction that would keep environmental pollution to a minimum.

It was found that the destruction of pesticides was generally aided by oxidizing agents. Binders were also found to be effective in their destruction, and it was discovered that the combination of oxidants and petroleum oil binders was no more effective than the oil binders alone.

By using polyethylene, which under heating or combustion conditions softens or degrades to products of lower molecular weight, the advantages of a liner and a binder were obtained with one material. A practical system was devised that consisted of burning the pesticide in a flattened polyethylene bag on or surrounded by other combustible material. Suggestions were made concerning an improved design of polyethylene container or liner to aid in carrying out the purpose of this investigation.

INTRODUCTION

The problem of the disposal of waste pesticides is constantly increasing in acuteness with the diversification of their use and the growth of population. Their escape into the environment as a result of disposal practices must be controlled or prevented. Some waste pesticides are being stored until safe disposal methods are available, however, they cannot be accumulated indefinitely. Various investigations leading to their proper disposal are presently being conducted.

A program conducted by the Environmental Health Sciences Center at Oregon State University, Corvallis, is in operation under the direction of R. L. Goulding. This project has as its objectives to develop a management system for the reduction of pesticide waste problems and to develop technical information concerning the treatment and disposal of these wastes. It is intended to utilize soil for biological and physical degradation of these wastes. Because this approach may offer an improved method of waste pesticide management, the U.S. Department of Health, Education, and Welfare's Bureau of Solid Waste Management (now the Office of Solid Waste Management Programs in the U.S. Environmental Protection Agency) is providing two-thirds of the cost for demonstrating and evaluating the concept through a grant to the university.

Another program in this field on the disposal of pesticides and containers is funded by a grant from the U.S. Department of

Agriculture and is administered through the Crops Research Division of the Agricultural Research Service. This is being conducted at Mississippi State University, College of Agriculture and Agricultural Experiment Station, State College, Mississippi, under the direction of B. J. Stojanovic, I. L. Shuman, and M. V. Kennedy, principal investigators. Some of the data obtained in the latter study are available in Residue Reviews.[7]

The present study was not concerned with the use of soil microflora as an aid in decomposition of pesticides in soils or with the development of an incinerator for disposal of pesticides and containers. Rather, it was oriented toward the use of oxidizers and binding agents as aids in the proper combustion of pesticides and containers. It was hoped that a practical, simple solution to the disposal of pesticide residues could be developed for use in the field.

OBJECTIVES OF THE PROJECT

The objectives of this investigation were the following:

1. To investigate the use of oxidizers and binding agents to assist in the combustion of pesticides
2. To investigate the combustion characteristics of container materials
3. To develop requirements for container compositions and possible use of special liners possibly impregnated with oxidizers to aid in the combustion of the pesticide and container

WORK PLAN

A. Research Program--Thermal Properties

    1. Obtain DSC instrument
    2. Operate with it as follows:
        a. Obtain decomposition temperature of pesticide
        b. Obtain thermal history of oxidants
        c. Obtain thermal history of binders
        d. Observe combinations of a, b, and c in closed systems
        e. Observe same operations in open systems
        f. Endeavor to get open system to imitate closed system by using binders, oxidants, or other additives

B. Research Program--Pyrolytic Studies

    1. Run crude pyrolysis experiments
    2. Investigate pyrolysis products by GLC
    3. Obtain Perkin Elmer pyrolyzer for use with PE 900 GLC
    4. Operate pyrolyzer as follows:
        a. Investigate the pyrolysis products of the pesticides
        b. Investigate the pyrolysis products of the oxidants
        c. Investigate the pyrolysis products of the binders

- d. Investigate the pyrolysis products of a, b, and c in combination
- e. Study combinations of pesticides, additives, and container materials
- f. Screen data for most promising combination

C. Research Program--Simulated Field Trials

1. Investigate packaging presently in use
2. Investigate combustion under simulated field conditions
   - a. Construct combustion test apparatus
   - b. Study effect of open flame on combustion
   - c. Apply procedures to the promising combinations derived from pure and applied research programs
3. Determine completeness of combustion by using the appropriate additives, packaging, and operational system
4. Prepare recommendations for combustible containers and operational procedure

THERMAL DEGRADATION OF PESTICIDES

It is known that chlorine-containing pesticides are the most difficult pesticides to decompose by combustion with air. DDT, for example, is used in burning fumigant mixture.[1,2] Some investigators have decomposed pesticides containing organic chloride by the following methods:

1. Treatment with steam and air at 900 to 1,400 C[3]

2. The addition of ferric chloride to accelerate thermal decomposition of DDT[4] and DDD[5]

3. Pyrolysis of pesticide with metal salt catalysts in a closed system[6]

Pesticides have been burned in oxygen in a dry combustion furnace,[7] but this does not serve the purpose of this investigation, which is to find a practical procedure for disposal of pesticide residues and the containers. The same authors also ashed pesticides in a muffle furnace.[7] This procedure imitates results that may be obtained by furnace destruction of residues and containers but may not be representative of open-field destruction, which is the principal means used to destroy combustible containers and their contents.

Thermal analysis by differential scanning calorimetry was able to provide theoretical data that it was hoped could then be used in practical pyrolytic procedures.

A useful pyrolysis unit had to meet the following requirements.

1. The sample should be reproducibly heated to a defined temperature.

2. The atmosphere in which pyrolysis occurs should be controlled.

3. The reaction chamber should be designed to permit convenient and complete sampling of the reaction products.

Pyrolysis Unit

The Perkin Elmer pyrolysis unit met these requirements (Figure 1). The weighed sample of pesticide was placed in a porcelain boat. The reaction atmosphere was air flowing at 30 ml/min. The decomposition products were formed when the boat was placed under the heated quartz tube area, and the temperature of degradation was measured with a thermocouple. The flowing air then swept all the reaction products into a Perkin Elmer gas chromatograph for analysis.

Pyrolysis of Pesticides

Screening of DDT and Malathion via gas liquid chromatography.

Temperature profile of DDT. A temperature profile of DDT from 250 to 900 C (Figure 2) indicates, in a gross manner, that the higher boiling isomers of the DDT (tech)

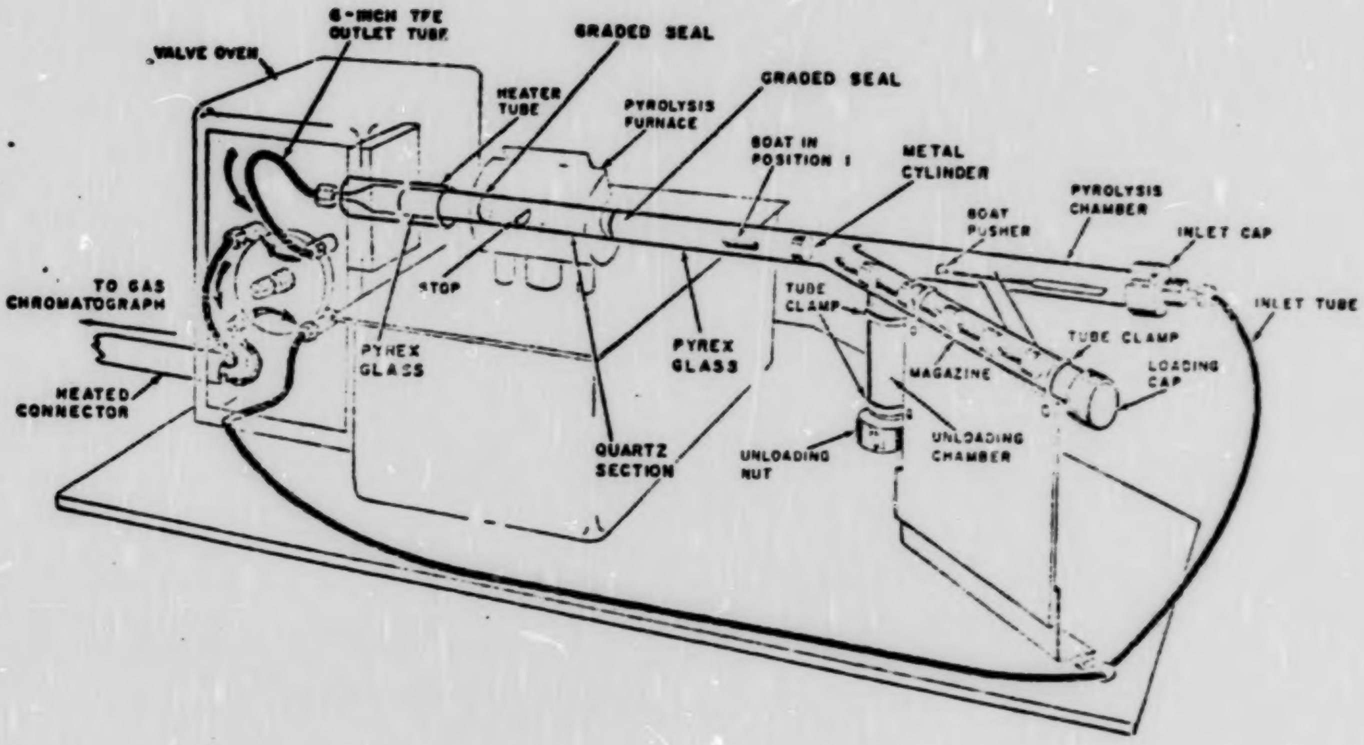
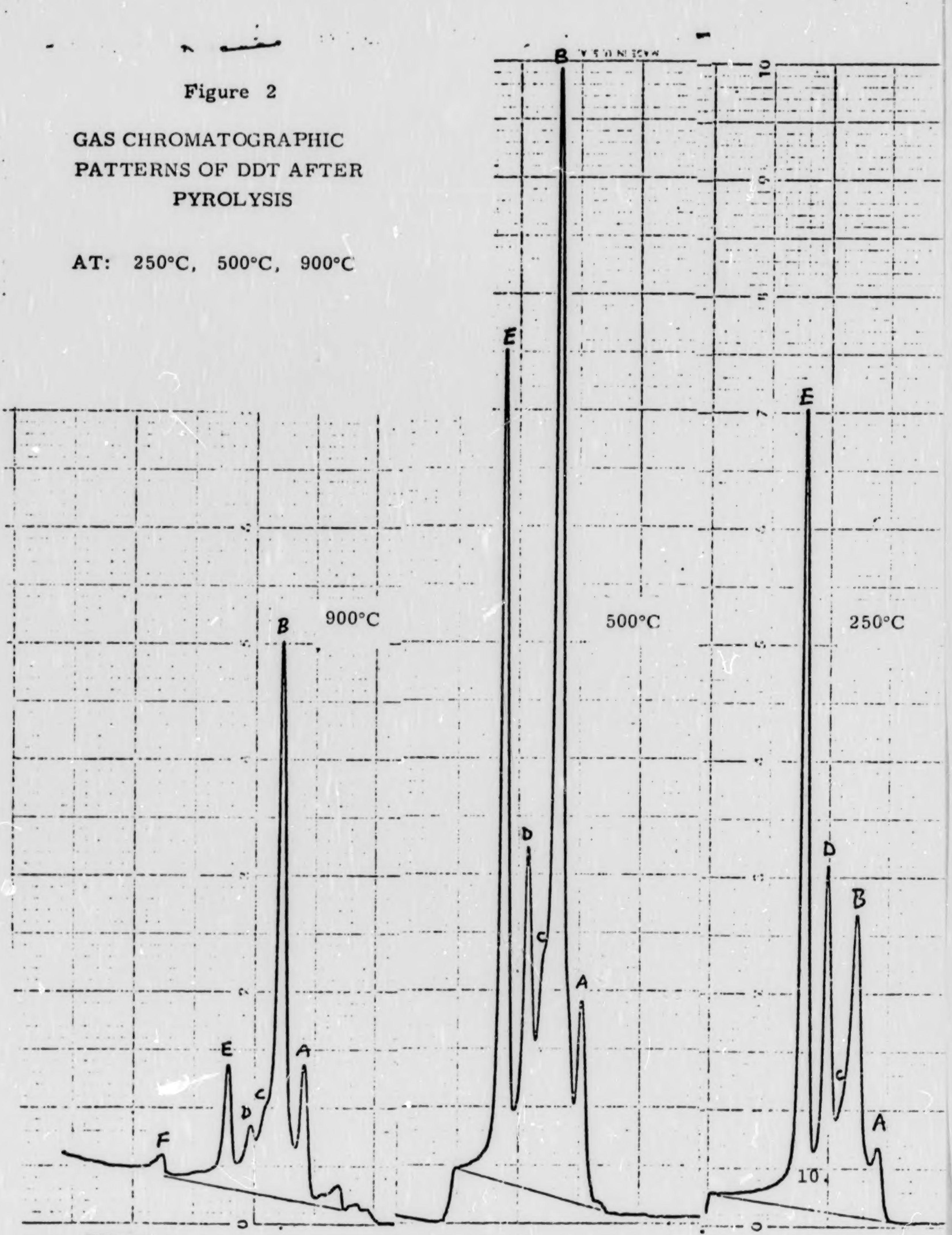


Figure 1. Schematic diagram of pyrolysis accessory (rear view). Arrows at valve indicate carrier gas flow with valve in OPERATE

Figure 2

GAS CHROMATOGRAPHIC
PATTERNS OF DDT AFTER
PYROLYSIS

AT: 250°C, 500°C, 900°C



mixture degrade rapidly to lower boiling compound as temperature increases. For example, the major component E, at 250 C, decreases as temperature increases while peaks A and B increase. A measure of this decomposition is expressed by the ratio of peaks A to E. The ratio at 250 C is 0.1/1; at 500 C it is 0.2/1; at 900 C it is 1.1/1.

The reproducibility of these gas liquid chromatography measurements was compared with samples of varying size having been pyrolyzed at 500 C (Table 1). The percent deviation from the mean for the three measurements was ±20. These data also indicate that sample size has an effect on reproducibility. The normalized peak heights of samples I and II, which are of equal size, were extremely reproducible. Their peak-height measurements differed markedly from sample III, which was seven and one-half times larger.

These data indicate that the system was reproducible enough to distinguish differences in gas liquid chromatography patterns greater than 20 percent when the pyrolysis temperature was 500 C. The data also indicate that increase in decomposition of DDT was a direct function of temperature, other things being constant.

Peak figures represent the ratio of a component relative to peak E set at 1.00 (Table 2). Peaks A and B, which represent decomposition products, have lower values when the oxidant is present than when it is absent. This indicates that under the conditions of the experiment the oxidants retarded rather than assisted decomposition.

TABLE 1

GAS CHROMATOGRAPHIC DATA--REPRODUCIBILITY OF DDT PYROLYZED AT 500 C.

	Peak heights*				Major peak
	A	B	C	D	
Retention time (min)	30.8	31.8	32.6	33.6	
Sample I (0.20 mg)	0.23	1.00	0.44	1.00	B
Sample II (0.20 mg)	0.24	1.4	0.41	1.00	B
Sample III (1.5 mg)	0.34	1.9	0.63	1.00	B
Mean	0.27	1.4	0.49	--	
Deviation from mean (%)	17	21	18	--	

*Normalized to 1 mg DDT and relative to the height of peak E.

TABLE 2

GAS CHROMATOGRAPHIC DATA--DDT PYROLYZED AT 500 C WITH OXIDIZING AGENTS

Sample of DDT	Oxidizing agent	Peak height*					Major peak
		A	B	C	D	E	
Retention time (min)		30.8	31.8	32.1	32.6	33.6	
I (1.0 mg)	Sodium nitrate	0.16	0.57	----	0.50	1.00	E
None	Sodium nitrate			None detected			
II (0.9 mg)	Potassium nitrate	0.15	0.81	----	0.44	1.00	E
None	Potassium nitrate			None detected			
III (1.0 mg)	Potassium chlorate	0.15	0.64	----	0.44	1.00	E
None	Potassium chlorate			None detected			
Mean DDT sample calculated from Table 1	None	0.27	1.4		0.49	1.00	B

*Normalized to 1 mg DDT and relative to the height of peak E.

Temperature profile of malathion. A temperature profile of malathion from 200 to 900 C is presented (Figure 3). As the temperature increased, peak C, which represents malathion, degraded to yield lower boiling peaks A and B. The ratio of peak A to C is an expression of the quantity of degradation. This ratio at 200 C is 0/1; at 500 C it is 1/1; at 900 C it is 15/1. These data indicate that rapid decomposition occurred at temperatures of 500 C or greater. No residue was detected at 200 C; a slight brown residue was detected at 500 C; and a large black residue was detected at 900 C, which indicates much carbonization.

The effect of oxidants on the decomposition of malathion. When milligram quantities of malathion were mixed with oxidants and pyrolyzed at 500 C the following results were observed for a minimum of two experiments per oxidant:

Oxidizing agent	Peaks detected	Sample residue	Explanation of results
Potassium chlorate	None	Yellow	Complete decomposition of malathion to oxides of carbon and water
Potassium nitrate	Major peak disappeared with formation of lower boiling components	Potassium nitrate	Complete decomposition of malathion to lower boiling components

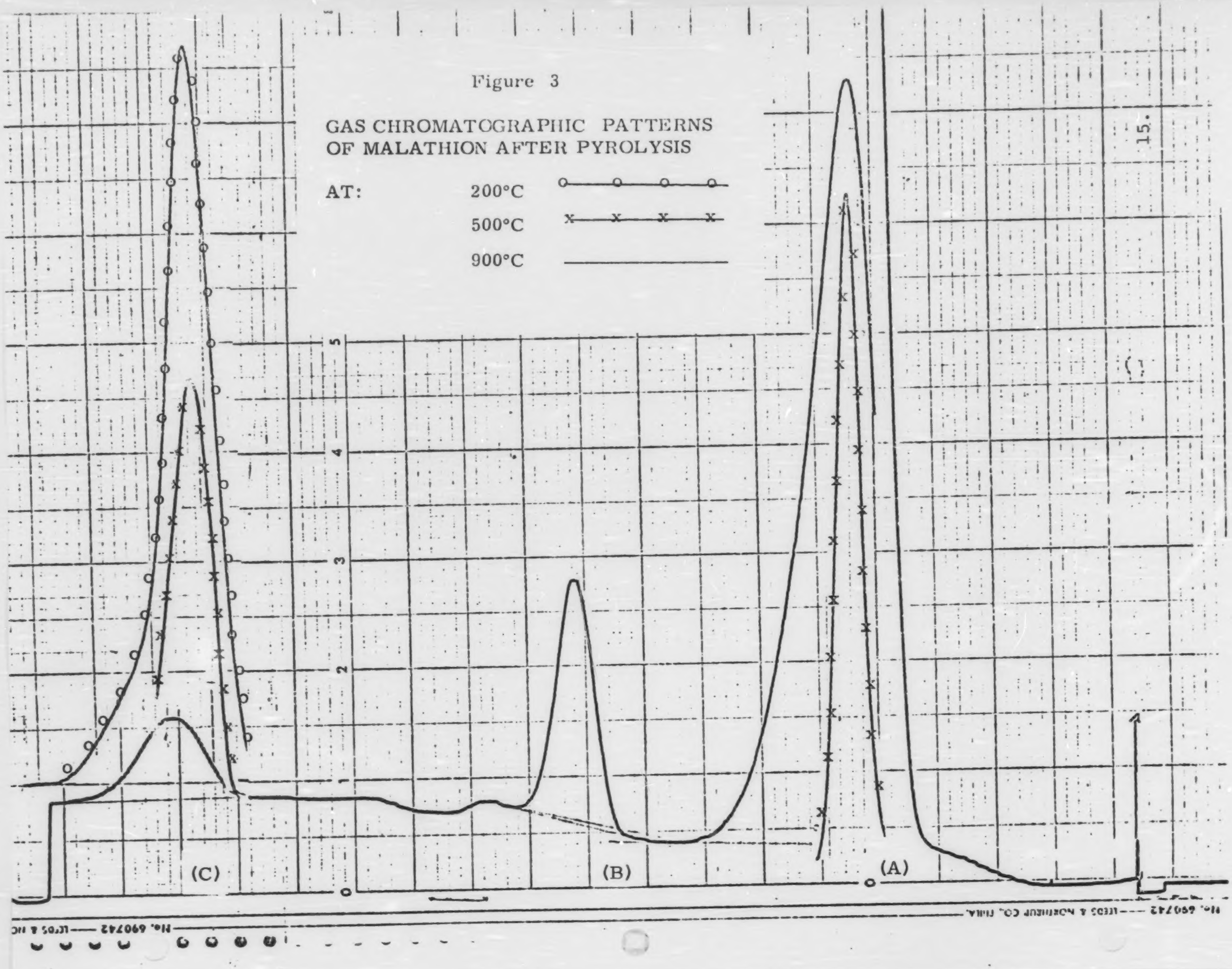


Figure 3

GAS CHROMATOGRAPHIC PATTERNS OF MALATHION AFTER PYROLYSIS

Modification of the Perkin Elmer Pyrolysis Unit

The Perkin Elmer pyrolysis unit had two flaws in its construction as follows:

1. The valve oven and heated connector could not be heated above the melting point of the Teflon tubing used to conduct the pyrolyzate to the gas chromatograph. Condensates collected in the valve and heated inlet tubing.

2. The heated connector to the gas chromatograph was subject to breakage. This section was replaced twice in a short period.

In order to overcome these design flaws, the end of the pyrolysis tube was disconnected from the valve and connected directly to the gas chromatograph via 1/8-in. stainless steel tubing. The tubing was wrapped with heating tape, and a thermocouple was imbedded next to the tubing. The entire assembly was then coated with asbestos for insulation. The temperature of this connecting line was maintained at 200 C.

When samples of pesticides alone were heated at relatively low temperatures (150 C), very small amounts of the pesticides were detected. It was assumed that the hot steel surface's being in the presence of air was responsible for the poor recovery. Modification was, therefore, made as discussed later.

Differential Scanning Calorimeter

The Perkin Elmer differential scanning calorimeter (DSC) used in the work to be described consisted of the following:

Item

- Calorimeter including temperature-programming unit
- Sample-handling unit
- Filter dryer for gas purge filtration
- Inlet line assembly
- Sample pan crimper press
- 120 VA constant-voltage transformer
- Plug-in sample holder
- Recorder with 15, 60, and 240 in./hr speeds
- Range card for 10-mv recorder
- Volatile-sample sealer accessory with sample pans and covers
- Manual

Theory of Operation. The sample holder of the DSC unit consists of two miniature pans, a reference and a sample pan (Figure 5). The pesticide was encapsulated in aluminum and placed in the sample pan. Aluminum ballast was placed in the reference pan. Heat was supplied to both pans at a constant rate to raise their temperatures 20 C/min. When a physical or chemical change took place in the sample pan, the heat generated or absorbed to complete this reaction was sensed by a platinum resistance thermometer embedded under that pan. Heat was then supplied to the sample pan if the reaction was endothermic (fusion, vaporization, etc), or heat was withheld if the sample reaction was exothermic (chemical reaction, decomposition, oxidation, etc). This change in power required to maintain the sample holder at the same temperature as the reference holder during the transition was the differential power and was recorded as a peak (Figure 4). The temperature of the transition was recorded on the curve abscissa as a pen stroke for each degree Centigrade. The recorded peak area indicated the total energy transferred to or removed from the sample. The reference pan should generate no signal, since the aluminum ballast had no transition below 660 C, its melting point. All signals generated in these experiments were attributed to reactions of the sample.

Peaks registered below the base line are endotherms and those above the base line are exotherms. The gradual change of base line slope was attributed to the change of the sample's specific heat as a function of temperature.

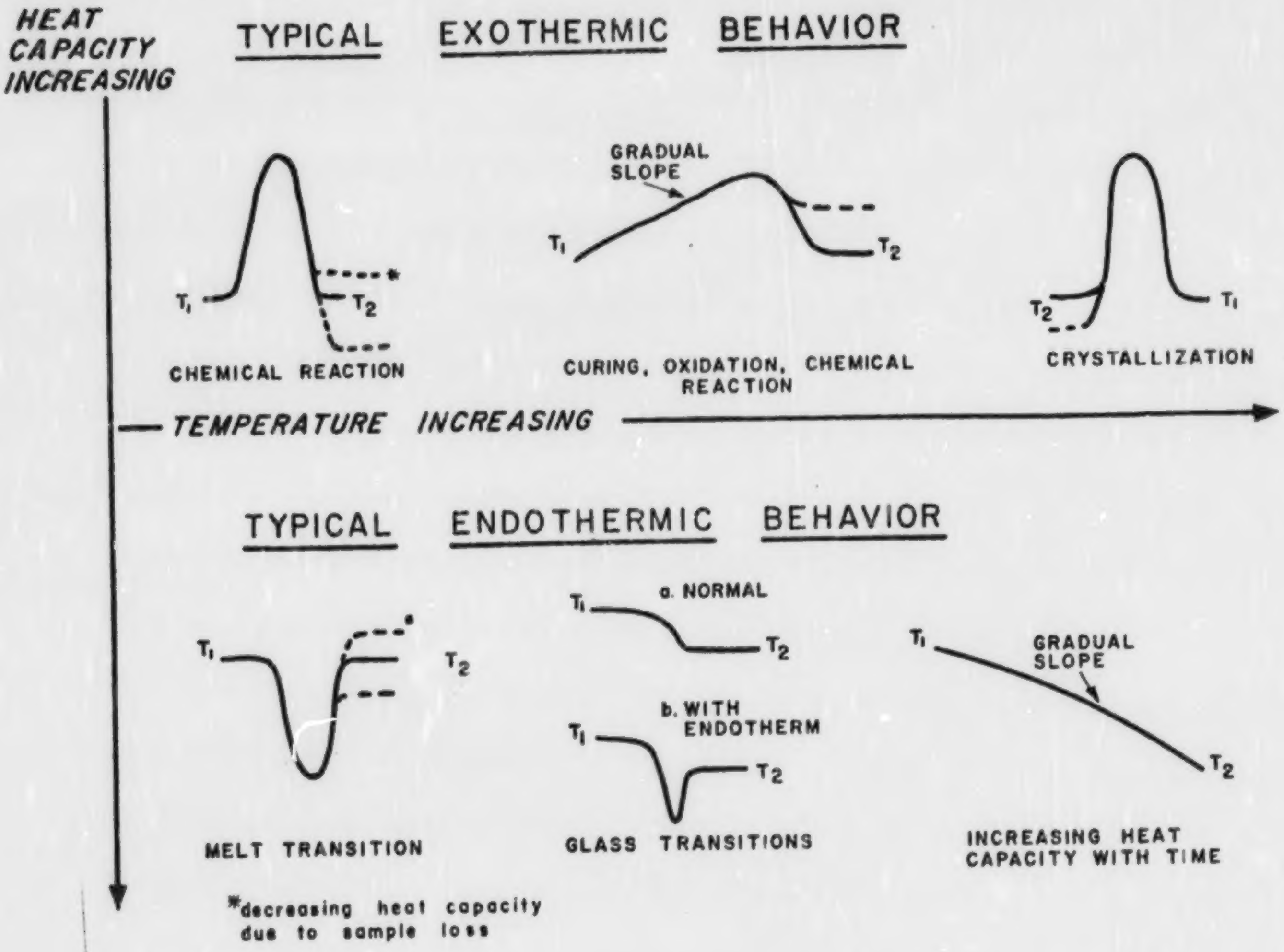


Figure 4. Typical chart indications of endothermic and exothermic transitions. (Asterisk indicates decreasing heat capacity due to sample loss.)

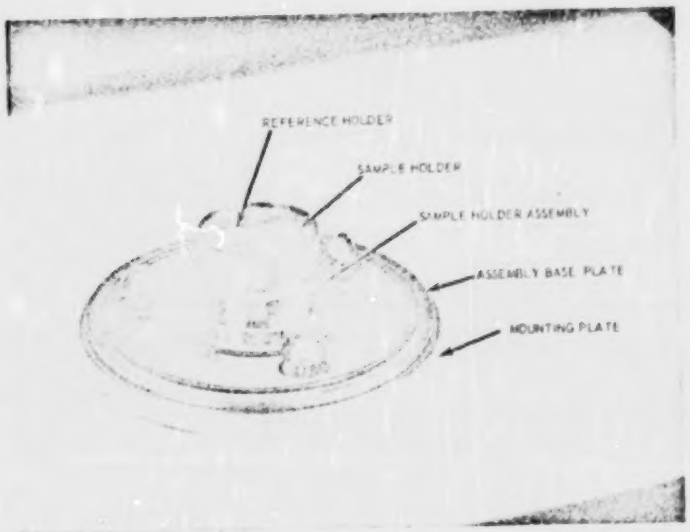


Figure 5. Sample holders in sample holder assembly.

Closed-System Operation. The sample was encapsulated in a volatile sample pan (Figure 6), and this permitted the major portion of the sample to decompose.

Many organic compounds, such as pesticides, will sublime or vaporize before the energy input is sufficient to decompose them. The effect of heating a sample of camphor in an open and closed system is illustrated (Figure 7). In the open system the major portion of the sample has sublimed before fusion. In the closed system the heat of fusion was accurately determined.

As the camphor sample was heated in the closed system, increased vapor pressure caused the sample pan to rupture. A microscopic pinprick was, therefore, made in the cover of each sealed pesticide sample pan to prevent rupture. Only a small portion of the pesticide volatilized when this procedure was employed. Some oxidation of the sample may be attributed to the diffusion of air through this pinhole.

Materials

DDT--technical grade, 77 percent pure, American Association of Economic Entomologists, Madison, Wisconsin. WO20551

Aldrin--99+percent recrystallized analytical grade, Jules Hyman and Co., Denver, Colorado. Lot 8001

Diazinon--50 percent wettable powder, Geigy Chemical Corporation, Ardsley, New York. FL 6423

Dalapon--99 percent analytical standard, Dow Chemical Company, Midland, Michigan. AGR20073

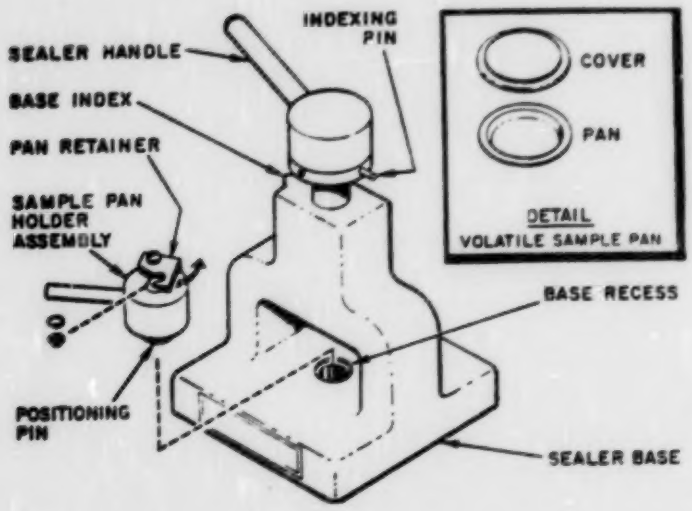


Figure 6. Sealer operation.

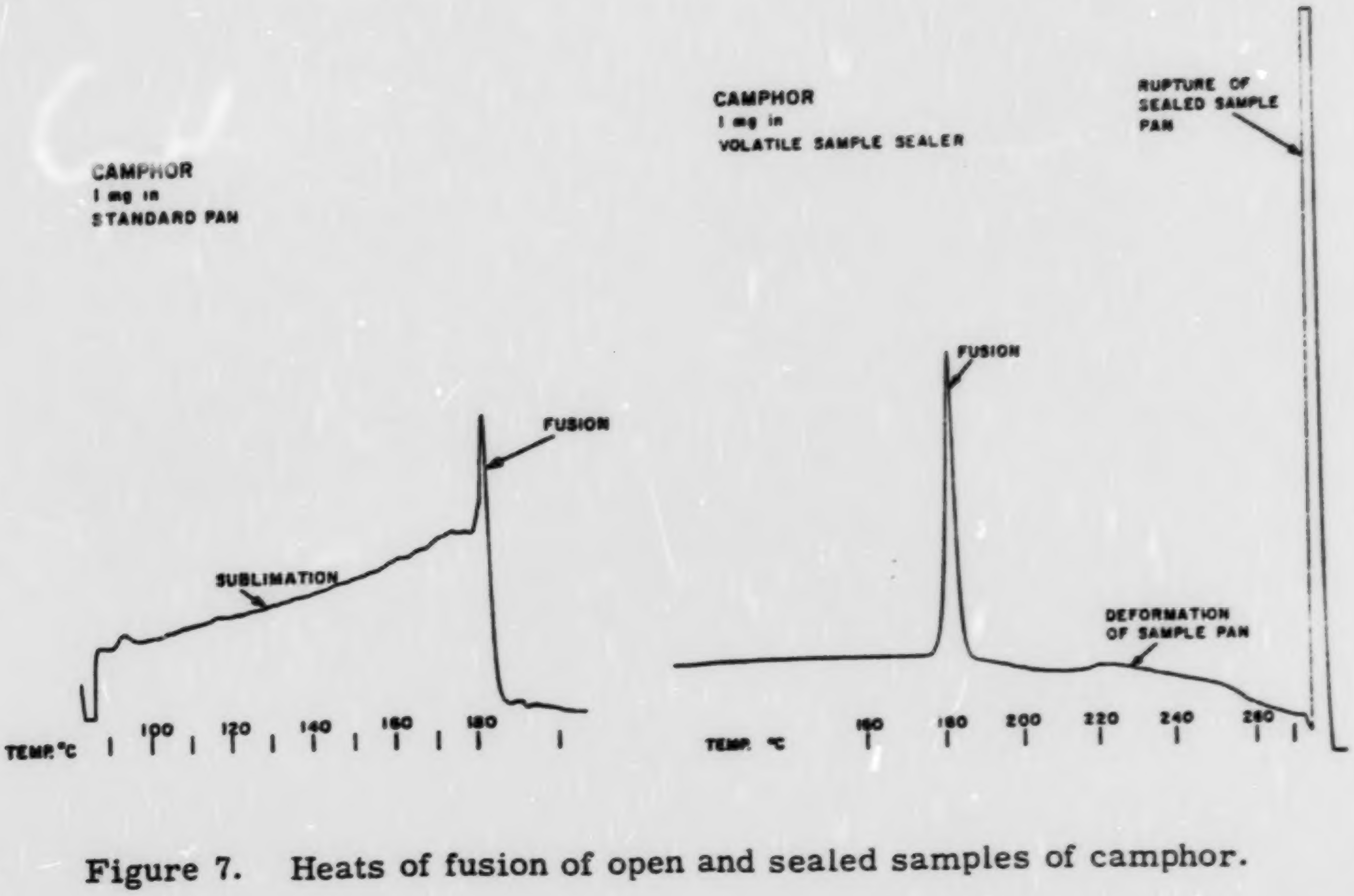


Figure 7. Heats of fusion of open and sealed samples of camphor.

Amino triazole--99.4 percent 3-amino-1,2,5 triazole, American Cyanamid Co., New York, New York. 3671B-32-2

Sevin--99.86 percent analytical grade, Union Carbide Co., New York, New York. Lot 14-ORD-18

Maleic hydrazide--58 percent diethanolamine salt of maleic hydrazide, MH-30, Uniroyal Chemical, Naugatuck, Connecticut. Lot 2281

Malathion--95 percent analytical reagent, American Cyanamid Co., New York, New York. Lot W-10628-2

Potassium nitrate--99 percent analytical reagent, Mallinckrodt Chemical Works, New York, New York. Lot 7028

Potassium chlorate--Mallinckrodt Chemical Works, New York, New York. Lot 6834

Pentachloronitrobenzene (PCNB)--Aldrich Chemicals, Cedar Knolls, New Jersey. P22C-5

Instrumental Conditions

Instrument--Perkin Elmer DSC
Scanning rate--20 C/min
Range (sensitivity)--16 to 64
Slope--426
Chart speed--1 in./min
Temperature range--67 to 500 C
Gas flow over sample--air at 20 ml/min
Sample:

Size--0.5 to 3.0 mg pesticide or oxidant, or both

Experimental Results. Pesticides without and with the addition of potassium nitrate and potassium chlorate, respectively, were scanned by closed-system DSC. The oxidants were also examined by DSC (Curves I-XXIX).

Decomposition or oxidation of the sample was defined as the production of an exothermic peak on the DSC curve. These decompositions were confirmed by examination of the sample for charring or ashing after the exotherm. The temperatures ranged from a maximum decomposition (Table 3). The initial temperature of decomposition was defined as the first departure from the base line. The final temperature of this range was defined as resumption of the base line.

The curves also contain first-order endotherms. Many of these peaks have been identified as either intercrystalline transitions or fusions based on the literature values for these transitions.

The data (Table 3) indicate the following for pesticides in a closed system:

1. The temperatures at which maximum decomposition of pesticides occurs can be measured.
2. The decomposition or oxidation of pesticides is accelerated when oxidants are present.
3. The presence of oxidants tends to decrease the temperature of maximum decomposition or oxidation.
4. Potassium chlorate is a better oxidizing agent for pesticides than potassium nitrate is.

TABLE 3

THE TEMPERATURE RANGE OF PESTICIDE DECOMPOSITION WITH AND WITHOUT OXIDANTS IN A CLOSED SYSTEM

	Decomposition temperature range (C)		
Compound	No oxidant	Potassium nitrate added	Potassium chlorate added
DDT	305-325	227-375	170-197 (major)
Aldrin	343-354 (minor) 383-403 (major)	294-500	304-331 (major) 349-359 (major) 438-457 (minor)
Dalapon	Exotherm not detected, but charring occurred	187-237	140-165 (major) 232-256 (minor) 317-362 (major)
Diazinon	256-(?) (at 294 pan exploded)	260-290 470-500	225-(?) (at 250 pan exploded)
Malathion	277-326	230-375	153-(?) (at 180 pan exploded)
3-amino-1,2,4-triazole	311-401	310-365 417-467	265-327
Sevin	277-367 (not clearly defined)	247-325	267-327
Maleic hydrazide diethanolamine salt (MH-30)	187-250 (not clearly defined)	Not evident, but charring occurred	182-(?) (at 226 pan exploded)
PCNB	No decomposition, no charring	No decomposition no charring	265-305

The DSC Screening of Pesticides in an Open System With and Without Potassium Chlorate

Open-System Operation. In the field, the burning of pesticides will take place in an open system where air will diffuse into the system and gaseous and vaporized products will leave the system. The following DSC conditions were used to approximate an open system:

1. The sample was weighed into a small aluminum pan. A thin aluminum disc was placed on top of the sample in the pan to ensure even heat distribution within the sample. The pan was not sealed--gases could diffuse into and out of the sample.
2. An atmosphere of air flowing at a rate of 20 ml/min was allowed to pass over the sample. Potassium chlorate was selected as the oxidant since it was most effective in the closed system.

Instrumental Conditions

Instrument--Perkin Elmer DSC
Scanning rate--20 C/min
Range (sensitivity)--16 to 64
Slope--400
Chart speed--1 in./min
Temperature range--67 to 500 C

Gas flow over sample--air at 20 ml/min
Sample:

Size--0.6 to 2.7 mg pesticide or
oxidant, or both

Experimental Results. The DSC curves obtained from an open system are interpreted in the same way as DSC curves obtained from a closed system. In the open system, however, condensation, charring, and rapid movement of the pan contents could be visually observed when the pan was heated. The temperatures at which such events were seen are indicated in Curves XXX-XXXXVII.

The results of heating pesticides with and without an oxidant in an open system are summarized (Table 4).

In most cases where pesticides alone were examined, in the open system, condensation was noted on the interior of the apparatus. This condensation was coincident with an endotherm on the DSC curve, and this indicated that vaporization or sublimation of the pesticide had occurred.

The data from this experiment indicate the following:

1. Pesticides heated in an open system do not decompose but appear to vaporize or sublime.

2. The addition of potassium chlorate appeared to oxidize the following pesticides: maleic hydrazide, diazinon, malathion, and 3-amino-1,2-4-triazole.

TABLE 4

OPEN SYSTEM. EXOTHERM EVIDENT OR NOT EVIDENT. RANGE OF MAXIMUM DECOMPOSITION (C)

Compound	Alone	Potassium chlorate added
DDT	Not evident No charring	Not evident No charring
Maleic hydrazide	Not evident Charring occurred	200-250 (minor) 344-357 (major) Charring occurred
Aldrin	Not evident No charring	Not evident No charring
Dalapon	Not evident No charring	Not evident No charring
Diazinon	Not evident No charring	371-397
Malathion	Not evident No charring	191-215
3-amino-1,2,4-triazole	Not evident No charring	319-352
Sevin	Not evident No charring	Not evident No charring
PCNB	Not evident No charring	Not evident No charring

The DSC Screening of Binders For Use in an Open System

Selection of Binders. Binders were sought to retard the vaporization and promote decomposition of the pesticide. The binder was not to react with the oxidant and was to possess reasonable thermal stability. The following materials were examined:

Mineral oil--"Kaydol" (Sonneborn Chemical and Refining Company, White Oil Division, New York, New York)

Paraffin wax--(City Chemical Corporation, New York, New York)

Dow Corning 200 fluid--a methyl silicone--(Applied Science Laboratories, Inc., State College, Pennsylvania)

Carbowax 20 M--a polyethylene glycol (Applied Science Laboratories, Inc., State College, Pennsylvania)

SE-30--a methyl silicone rubber (Applied Science Laboratories, Inc., State College, Pennsylvania)

Apiezon M--hydrocarbon grease. (James G. Biddle Company, 1316 Arch Street, Philadelphia, Pennsylvania)

Polyethylene--Eastman Epolene N-10, Eastmen Epolene C-10.

Experimental Results. The instrumental conditions were the same as those used in the screening of pesticides in an open system. All the materials showed some evidence of volatility or decomposition. The following materials were selected for further testing because of their stability:

Dow Corning 200 fluid
Carbowax 20 M
Apiezon M
Mineral oil

These materials were analyzed by DSC with only potassium chlorate added, with only DDT added, and with only potassium chlorate and DDT added. The following results were obtained (Curves XXXXVIII-LII):

Dow Corning 200 fluid--The addition of this substance did not aid oxidation or decrease volatilization of the pesticide. No exotherm or charring was observed.

Carbowax 20 M--The potassium chlorate reacted with Carbowax 20 M. This type of reaction is undesirable since it competes with the oxidation of the pesticide.

Apiezon M--the Apiezon M reacted with potassium chlorate, and this made it undesirable as a binder.

Mineral oil--Potassium chlorate did not react with mineral oil. When both potassium chlorate and DDT were added to mineral oil, there was a large exothermic response that was interpreted as probable decomposition of the DDT.

The DSC Screening of Pesticides With and Without Potassium Chlorate and Containing Mineral Oil as a Binder

The addition of mineral oil to DDT and potassium chlorate appeared to aid oxidation in the open system. The remaining eight pesticides were screened in the same fashion to determine the effect of this binder (Curves LIII-LXVIII). The results of this screening are summarized (Table 5).

In every case the admixture of both potassium chlorate and mineral oil resulted in an exothermic reaction indicative of

TABLE 5

OPEN SYSTEM. EXOTHERMS EVIDENT OR NOT EVIDENT. RANGE OF MAXIMUM DECOMPOSITION (C) WITH AND WITHOUT POTASSIUM CHLORATE BUT WITH MINERAL OIL AS A BINDER IN ALL CASES

Compound	Alone	Potassium chlorate added
DDT	Not evident	270-325 (minor) 337-390 (major)
Maleic hydrazide	Not evident	231-258 (minor) 336-378 (major)
Aldrin	293-297 (very small)	334-369
Dalapon	Not evident No charring	336-364
Diazinon	257-305	288-318 350
Malathion	Not evident	154-221 332-345
3-amino-1,2,4-triazole	Not evident	267-315 312-345
Sevin	326-336 (small)	324-354 (small)
PCNB	312-315 (very small)	323-357

degradation. These data did not allow us to determine the exact reaction occurring or its extent. This information would be obtained when this system was tested by pyrolysis and gas chromatographic analysis.

The DSC Screening of Oxidants Other Than Nitrates and Chlorates in an Open System With DDT

Five oxidizers were tested with DDT only, mineral oil only, and with both DDT and mineral oil. DDT was selected as a test pesticide because it is relatively stable to oxidation.

Reagents

Potassium persulfate--Mallinckrodt analytical reagent
Ammonium bichromate--Fisher Scientific Company
Potassium permanganate--J. T. Baker Chemical Company
Sodium peroxide--J. T. Baker Chemical Company
Potassium dichromate--J. T. Baker Chemical Company

Instrumental Conditions

Instrument--Perkin Elmer DSC
Scanning rate--20 C/min
Range (sensitivity)--32
Slope--400
Chart speed--1 in./min
Temperature range--67 to 500 C
Gas flow over sample--air at 20 ml/min
Sample:

0.6 to 2.7 mg of DDT was weighed into an aluminum pan that was not sealed

Experimental Results. The following summarizes the results obtained in the experiments leading to the results shown by Curves LXIX-LXXXIV.

> Potassium persulfate--There was no evidence that the potassium persulfate reacted with the DDT alone or in admixture with mineral oil.
>
> Ammonium bichromate--There was no evidence that the ammonium bichromate reacted with the DDT alone or in admixture with mineral oil.
>
> Potassium permanganate--The potassium permanganate reacted with the mineral oil, which was used as a binder. Thus, it is an undesirable oxidant.
>
> Sodium peroxide--The sodium peroxide reacted with the aluminum pan. This made it impossible to obtain a DSC trace.
>
> Potassium dichromate--There was no evidence that the potassium dichromate reacted with the DDT alone or in admixture with mineral oil.

The results of these tests indicate that potassium chlorate is still the most suitable oxidizer investigated.

The Pyrolysis of Pesticides in the Presence of Mineral Oil and Potassium Chlorate

Apparatus. As reported, the Perkin Elmer pyrolysis unit was modified to measure the pyrolytic decomposition of pesticides. The unit was modified in the following manner:

1. The section of the pyrolysis tube between the furnace and the exit was kept at 200 C by means of heating tape.

2. A 10-cm length of Teflon tubing (1/8 inch OD) was attached to the end of the pyrolysis tube by means of a swagelok fitting.

3. The other end of the Teflon tubing was inserted into a U-shaped collector bottle (Varian Aerograph, Model 66-023, 1-ml size), which was clamped vertically in a dry ice/ethanol bath.

Air was passed through the apparatus at a known flow rate and for a definite length of time. At the end of the experiment, the collector bottle removed, and 0.5 ml of an appropriate solvent was added to the cold bottle. Portions of this solution were examined by means of gas chromatography to determine the amount of pesticide in the cold trap.

This method measured the effectiveness of the pyrolysis, since the amount of pesticide placed in the pyrolysis furnace was known. At the same time, any indication of the kind of degradation products on the gas chromatograms was noted. Gaseous products that would not respond to the hydrogen flame detector (such as carbon dioxide, water, or hydrogen chloride) could not be detected. Low-boiling organic compounds not separated from the solvent (diethyl ether or ethanol) were also undetected.

Instrumental Conditions

Perkin Elmer pyrolysis unit:

Furnace temperature: 300 C
Gas : Air at 100 ml/min
Collection period : 10 min

Gas chromatography:

Aerograph 705: Column: 4 ft x 1/8 in. OD stainless steel packed with 15% SE-30 on Gas Chrom P

Temperatures:

Column: as indicated
Detector: 220 C
Injector: 240 C

Carrier gas: Nitrogen at 25 ml/min

Aerograph 1520: Column: 3-1/2 ft x 1/8 in. OD stainless steel packed with 3% SE-30 on Gas Chrom P

Temperatures:

Column: as indicated
Detector: 220 C
Injector: 240 C

Carrier gas: Nitrogen at 25 ml/min

Sample size: Equal amounts (2-4 mg) of each ingredient

All the pesticides studied were examined under these conditions. Dalapon, maleic hydrazide, and 2-amino-1,2,4-triazole, which are not gas chromatographable, were omitted. Atrazine was substituted for 3-amino-1,2,4-triazole. A furnace temperature of 300 C was selected. Previous DSC studies showed that in the presence of both mineral oil and potassium chlorate, the pesticides would decompose at this temperature. Other flow rates of air and collection times were tried, but that selected, 100 ml/min for 10 min, gave the most consistent results.

Experimental Data. The chromatograms are shown in Curves LXXXV-CXIX. The results are summarized (Table 6).

Reproducibility of Results. Several replicate pyrolysis experiments were made with Aldrin in order to test the reproducibility of the method. The results are summarized (Table 7).

These results indicate that the method was adequate for determining significant changes in decomposition as the composition of the sample was varied. Similar results were obtained for replicate pyrolytic tests of Sevin and DDT.

Pyrolytic Degradation Products. DDT was the only pesticide studied that showed significant amounts of degradation products by gas chromatography that were not present in the chromatogram of the reference DDT. When DDT was pyrolyzed alone, the degradation products produced larger peaks than that for DDT itself. These unknown peaks were, however, greatly reduced in size in the gas chromatograms of the pyrolytic products of DDT plus either mineral oil or potassium chlorate.

TABLE 6

AMOUNT OF PESTICIDE RECOVERED IN DRY ICE/ETHANOL COLD TRAP AFTER PYROLYSIS AT 300 C

	Pesticide alone (%)	Pesticide plus mineral oil (%)	Pesticide plus potassium chlorate (%)	Pesticide plus mineral oil and potassium chlorate (%)	Gas chromatographic conditions
Sevin	50	5	25	5	Aerograph 1520--column at 135
PCNB	50	5	25	25	Aerograph 1520--column at 135
Aldrin	20	10	25	10	Aerograph 1520--column at 145
Diazinon	5	5	5	5	Aerograph 1520--column at 155
DDT	10	5	1	5	Aerograph 705--column at 190
Malathion	5	5	5	5	Aerograph 705--column at 160
Atrazine	5	5	5	5	Aerograph 1520--column at 140

TABLE 7

PERCENT OF ALDRIN RECOVERED IN DRY ICE/ETHANOL COLD TRAP AFTER PYROLYSIS AT 300 C

	Aldrin alone	Aldrin plus mineral oil	Aldrin plus potassium chlorate	Aldrin plus mineral oil and potassium chlorate
1st	60	15	30	10
2nd	17	10	24	0
3rd	20	0	0	0
4th	20	0	0	0

Conclusions

The addition of mineral oil to either Sevin, Aldrin, PCNB, or DDT significantly increased the amount of pesticide that decomposed when heated at 300 C. The mineral oil did not have a significant effect on the decomposition of either Diazinon, Malathion, or Atrazine at 300 C. These three pesticides were, however, largely decomposed by heat alone.

The addition of potassium chlorate to either Sevin, PCNB, or DDT increased the amount of pesticide that was decomposed at 300 C; it did not affect either Aldrin, Diazinon, Malathion, or Atrazine. In general, the addition of potassium chlorate to the pesticide had less effect than the addition of mineral oil.

The addition of both mineral oil and potassium chlorate to the pesticide had no greater effect than that of the addition of mineral oil alone. The addition of either mineral oil or potassium chlorate to DDT reduced the amount of gas chromatographable pyrolytic products of DDT.

THERMAL INVESTIGATION OF CONTAINER MATERIALS

Container Materials Study

Apparatus. A large tripod was set up and a wire screen placed over it. The ignition characteristics of container materials were observed by igniting the materials with a Bunsen burner until they were burning satisfactorily. The maximum temperature reached was measured by a pyrometer by moving it about in the burning mass and combustion gases throughout the combustion period. The temperature depended in part on the quantity of burning material but more on the rate of combustion and rate of loss of combustion products.

Materials Investigated

Kraft paper bag
Corrugated box
Paper-coated cardboard box
Fiberboard carton (small drum)
Corrugated sheet
Cotton cloth (diaper material)
Waxed paper bag
Polyethylene bag
Polystyrene cushion container
Plywood (1/8 in.)
Burlap bag
Cardboard carton

Multiwall paper bag
Aluminum foil inside coated paper bag used for packaging Diazinon
Aluminum foil inside coated multiwall Kraft paper bag used for packaging Diazinon
Coated double-wall Kraft paper bag used for packaging Igran
Multiwall coated Kraft paper bag used for packaging Altratol

Experimental Data

Burning Characteristics

A. The Kraft paper bag was crumpled before ignition. It was easily ignited, burned rapidly and well, and left a light, fluffy ash. When the bag was not crumpled and was left open, it was easily ignited, burned more rapidly than before, and left a light, fluffy ash.

b. A corrugated box (8 x 12 x 14 in.) was ignited at a corner. It burned with some smoke, rapidly and well, and left a large amount of ash.

c. A paper-coated cardboard carton was ignited fairly easily. It burned with a slow, steady flame and left a fair amount of residue.

d. A fiberboard carton (small drum) (2 in. high x 8 in. diameter) took some time to ignite. It burned slowly and steadily once ignited, smoked considerably, and left a large amount of ash. After the flame ceased, it glowed for some time.

e. A corrugated sheet ignited readily, smoked initially, but after it was burning well, the smoke ceased. There was a fair amount of ash.

f. The cotton cloth was crumpled. It ignited easily, burned steadily but not rapidly. As the flame decreased, the smoke increased. A black residue remained. When burned without crumpling, it burned much more rapidly.

g. A waxed paper bag ignited very easily and burned rapidly to completion.

h. A lightweight polyethylene bag burned slowly with a blue and yellow flame, melted, and dripped as it burned. It was initially difficult to ignite, but once the melt was obtained, it continued steadily on its own. A heavier gauge bag was even more resistant to initial ignition, but once melted, it likewise maintained its own combustion for a long period.

l. A polystyrene cushion container ignited easily, burned rapidly, but produced a great amount of black smoke and soot. It dripped as it burned and produced much styrene monomer, detected by odor, which also burned.

j. A plywood panel was difficult to ignite. It burned slowly but not completely and left a large amount of charred wood.

k. A burlap bag (dual layer) burned rapidly, producing much white smoke and leaving a fair amount of ash.

l. A cardboard carton was slow to ignite, but once ignited, burned at a slow, steady rate. It left considerable ash, leafy residue, and tarry residue. Once the flame had died out and it had been reignited, it did not burn well.

m. A multiwall paper bag ignited readily and burned well and rapidly with very little smoke. It left only a small ash.

n. An aluminum-foil-coated bag burned rapidly with a moderate amount of smoke and left much ash and aluminum residue.

o. An aluminum-foil-coated, multiwall bag burned at a moderate rate, gave a moderate amount of smoke, and left a large amount of ash.

p. A coated, double-wall Kraft paper bag burned at a moderate rate with some smoking and left a fair amount of residue.

q. A multiwall, coated Kraft paper bag burned rapidly with little smoke and left a small amount of residue.

Maximum Combustion Temperature

Item	Temp (C)	Temp (F)
a	542	1,025
b	627	1,160
c	621	1,150
d	496	925
e	627	1,160
f	691	1,275
g	579	1,075
h	607	1,125
i	593	1,100
j	638	1,180
k	593	1,100
l	621	1,150
m	621	1,150
n	579	1,075
o	579	1,075
p	579	1,075
q	593	1,100

Pesticide Combustion Apparatus

A series of experiments was carried out to determine the best arrangement for burning pesticides in packaging containers and collecting the gases for analysis. The equipment had to imitate open-air combustion as closely as possible. By allowing free access of air in the absence of drafts, it was possible to arrange for free combustion and yet collect the off-gases and still avoid possibly being poisoned by vaporized pesticide. This was accomplished by installing the setup in a hood, operating with the fan off, and having the operators use gas masks.

An aluminum pan was placed on a wire gauze on a ring held on a large stand. A 14-in. diameter, galvanized funnel was inverted and suspended 1 in. above the aluminum pan. The stem of the funnel was connected to pyrex connectors that led by a glass system, joined by Teflon to a gas-scrubbing bottle with fritted disc containing 200 ml ethanol, then to a trap, and then to an air suction pump.

Trial experiments showed that a successful combustion could be carried out in this apparatus with multiwall Kraft paper.

THERMAL DESTRUCTION OF PESTICIDES IN CONTAINERS

A Practical System For Pesticide Combustion

Work previously discussed has indicated that mineral oil is a very satisfactory binding agent. Other data showed that chlorate was the most suitable oxidizer. When the data thus obtained by differential scanning calorimetry were applied to pryrolysis experiments, it was found that the oxidizer was not necessary.

The mineral oil is very important since it holds the pesticide until it can be decomposed by heat before volatilizing. It was felt that thoroughly wetting all particles of pesticide could not be accomplished in a practical way, and so a scheme was devised to accomplish the same result.

Mineral oil essentially consists of hydrocarbons having chains of moderate length. Polyethylene is a polymer of ethylene that consists of very long-chain hydrocarbons. When polyethylene is heated it partially depolymerizes to shorter chain hydrocarbons that are roughly similar to mineral oil It was felt that, by using polyethylene bags as liners to contain the pesticide, the same result obtained by using mineral oil as a binder could be achieved.

Experiments were carried out in the apparatus for collecting combustion gases, as described under Pesticide Combustion Apparatus. The results are given in the next section. As a consequence of the work, a system for practical combustion of waste pesticides can now be described.

Pesticides should be shipped in containers having an inner polyethylene bag to hold the pesticide. When the pesticide is used or the container emptied, the bag should be left in place. When it is desired to destroy the container and avoid air or ground contamination by the residue of pesticide, the entire carton or bag may be burned if it is combustible. If it is not combustible, the bag containing the residue should be removed and placed on top of other combustibles at the desired location for burning. The other combustibles may be a sufficient supply of paper, cardboard cartons, or wood.

In either case, the polyethylene bag should be flattened or closed in such a way as to avoid enclosing any considerable amount of air. This should be done because air will tend to inflate it, and when the flame and heat melt it, a hole will appear and the gases will carry residue away. In contrast by collapsing the bag, the polyethylene melts when heat reaches it, and breaks down to a sticky, gummy mass that successfully holds the residue until it is completely consumed.

It is important to have sufficient other combustible material present to keep the polyethylene ignited in the early stages. When it is finally melted down thoroughly to a molten mass, it will continue to burn for a considerable period and destroy all residue.

It appears that the most satisfactory container for residue destruction is a multiwall bag containing a polyethylene inner bag. The inner bag should not be simply a polyethylene coating but a separate container. It is preferable not to use aluminum foil or coating, since this hampers combustion and heat transfer.

Where shipments are to be made in cartons or combustible drums, the same polyethylene liner should be used. If the drum is to be saved, the bag can be removed and burned on top of other combustibles, as stated before.

The polyethylene liner should not be of too heavy gauge, since this hampers closing or folding it to exclude air, and it takes too long to melt it, and hence, if a hole is burned in it, some residue may escape by volatilization before being held and destroyed. A gauge of 1 to 10 mils appears suitable.

If the pesticide is a liquid, it could be shipped in packages consisting of a flexible polyethylene inner container encased in a corrugated carton (Poly Pac type). This would be suitable for 1- to 5-gal quantities, and it could be destroyed in the manner previously described. The polyethylene container would of necessity be of heavier gauge than the usual lightweight bags or liners. It would still, however, be flexible and could be flattened before combustion in its carton.

If the pesticide cannot be shipped in polyethylene but can be shipped in a combustible container, then mineral oil should be used to wet the pesticide residue before combustion. Of course, this can also be done, if desired, when the container is polyethylene.

Pesticide Combustion Gases

Initial experiments to set up and test the combustion and collection equipment were all performed with DDT. The final arrangement for the laboratory tests for simulating a practical procedure consisted in placing the pesticide in a polyethylene bag, folding or crumpling the bag together to eliminate air, and placing it on torn pieces of multiwall bag in an aluminum pan beneath an inverted funnel. The multiwall bag sections were ignited with a Bunsen burner and the gases drawn by the vacuum pump into 200 ml of ethanol. After the combustion was completed, any residues that may have condensed in the equipment were washed off with alcohol and the alcoholic portions combined. The alcohol solution volume was measured and then, where suitable, subjected to gas chromatographic analysis for determining the presence of the pesticide or decomposition products collected.

It would have been preferable to have perforations in the bottom of the aluminum dish to aid combustion. This could not be done, since the melted polyethylene ran through and the gases escaped the funnel. In practice, this would not be a problem, since gases would not be collected.

Experimental Data

Legend

258A	1.0 g DDT in polyethylene on multiwall Kraft
258B	1.0 g DDT plus mineral oil in polyethylene on multiwall Kraft
258C	1.0 g DDT on multiwall Kraft
258D	1.0 g DDT burned alone

Combustion stopped intentionally before complete:

	%
Recovered as residue (no DDT present)	32.6
DDT recovered in alcohol	0.5
Decomposition products recovered in alcohol	12.5
DDT totally destroyed	54.4

260A	1.0 g Aldrin on multiwall Kraft
260B	1.0 g Aldrin in polyethylene on multiwall Kraft

Incomplete combustion due to insufficient air

261A	2.0 g Diazinon 50W (50% wettable powder) in polyethylene on multiwall Kraft
261B	0.5 g PCNB in polyethylene on multiwall Kraft
261C	0.5 g Sevin in polyethylene on multiwall Kraft
261E	0.5 g Atrazine in polyethylene on multiwall Kraft
261I	0.5 g Malathion in polyethylene on multiwall Kraft
261D	0.5 g 3-amino-1,2,4 triazole in polyethylene on multiwall Kraft
261F	0.5 g 2,4-D acid in polyethylene on multiwall Kraft
261G	0.5 g MH-30 (maleic hydrazide) in polyethylene on multiwall Kraft
261H	0.5 g Dalapon in polyethylene on multiwall Kraft

In the cases of 261D, F, G, and H, the pesticide itself was not detectable by gas chromatography. The method was applied to search for volatile decomposition products, but none were found.

Pesticide	Run	Recovered in alcohol (%)	Minimum detectable (%)	Decomposition products
DDT	258A	NF	0.5	NF*
DDT	258B	NF	0.5	NF
DDT	258C	NF	0.5	NF
DDT	258D	0.5	0.5	12.5
Aldrin	260A	NF	0.1	NF
Aldrin	260B	0.3	0.1	NF
Diazinon	261A	0.2	0.2	NF
PCNB	261B	0.5	0.5	NF
Sevin	261C	NF	1.0	NF
Atrazine	261E	NF	0.5	NF
Malathion	261I	NF	0.5	NF
Amino triazole	261D	---	---	NF
2,4-D	261F	---	---	NF
MH-30	261G	---	---	NF
Dalapon	261H	---	---	NF

---

*NF denotes Not Found.

Analysis for 261D, F, G, and H. Since four of the pesticides were not detectable by gas liquid chromatography, the alcoholic solutions of each were analyzed by thin-layer chromatography.

Thin layer plates:	silica gel F254 (Brinkman Instruments, Inc)
Irrigant:	n-butanol, acetic acid, water-60/15/25

Visualizing agents:

Short-wave ultraviolet light

Sodium salt of dichloroindophenol

Pesticide	Test plates Rf	Minimum amount detectable (μg)
Amino triazole	0.40	30
2,4-D	0.65	30
MH-30	0.60	30
Dalapon	0.55	60

When first tested, each of the alcohol solutions gave a negative test for the sought pesticide. In order to increase the sensitivity of the tests, 100-ml portions of the alcohol solutions were concentrated by evaporation, under nitrogen on a hot water bath. The concentrates were tested at two stages, 20-fold and 200-fold concentrates.

The maximum amount of pesticide the solutions could have contained was 0.5 g or 2.5 μg/μl. For 20 x concentration this is 50 μg/μl. When 12 μl was spotted, each application contained 600 μg. The minimum sensitivity was 30 μg 30/600 x 100 = 5 percent except for Dalapon. This method could detect 5 percent of the maximum amount that could be present. For 200 x concentration 0.5 percent could be detected.

All the concentrates gave a negative test for the sought pesticide. In addition, there were no spots on the TLC plates, and this finding indicated absence of breakdown products of the pesticides.

Pesticide	Amount pesticide burned (g)	Amount detected alcohol in trap	Minimum amount detectable
Amino triazole	0.500	NF	0.0025 g (0.5%)
2,4-D	0.500	NF	0.0025 g (0.5%)
NH-30	0.500	NF	0.0025 g (0.5%)
Dalapon	0.500	NF	0.0050 g (1.0%)

The data obtained showed that no more than 0.5 percent (in the case of Dalapon, 1.0 percent) of any of the pesticides teated by the preferred procedure escaped as undecomposed vapor. In a practical situation the proportion of pesticide to combustibles would be much smaller than was employed here (1:7). The likelihood of loss by vaporization would then be much lower.

End Product Gases. It is known that carbon monoxide and carbon dioxide are formed by burning cellulose or polyethylene, and this can be easily shown. Omitting these gases from consideration, the following tabulation shows the simple gases that might be formed by burning the pesticides and is based on their respective structural formulas. The pesticides were burned in polyethylene bags and the gases analyzed with the results shown.

Gaseous Products

Pesticide	Possible	Found	Not found
DDT	Hydrogen chloride	x	
	Chlorine		x
	Chlorine dioxide		x
	Phosgene		x
Aldrin	Hydrogen chloride	x	
	Chlorine		x
	Chlorine dioxide		x
	Phosgene		x
Dalapon	Hydrogen chloride	x	
	Chlorine		x
	Chlorine dioxide		x
	Phosgene	x	
Diazinon	Hydrogen sulfide	x	
	Sulfur dioxide	x	
	Ammonia		x
	Nitrogen dioxide		x
Malathion	Hydrogen sulfide	x	
	Sulfur dioxide	x	
3-amino 1,2 4-triazole	Ammonia	x	
	Nitrogen dioxide		x
Sevin	Ammonia		x
	Nitrogen dioxide		x
Maleic hydrazide diethanolamine salt (MH-30)	Ammonia	x	
	Nitrogen dioxide		x
PCNB	Hydrogen chloride	x	
	Chlorine	x	
	Chlorine dioxide		x
	Phosgene	x	
	Ammonia		x
	Nitrogen dioxide	x	

CONCLUSIONS AND RECOMMENDATIONS

1. Pesticides may be destroyed by combustion at the temperatures normally achieved by burning wood, paper, cardboard, or plastics.

2. The combustion products are mainly end products of combustion such as carbon dioxide, carbon monoxide, sulfur dioxide, chlorine, ammonia, hydrogen sulfide, hydrogen chloride, and phosgene.

3. Only small or negligible amounts of intermediate products of combustion are formed.

4. The original pesticide, is more than 99 percent destroyed.

5. Pollution by end products such as sulfur dioxide and hydrogen chloride would depend on whether or not they are formed by the pesticide and on the quantity of pesticide destroyed. Since only residues are being burned and only a fractional amount of pollutant is formed, normal burning of a few containers would involve negligible pollution. This would not apply to collection centers where the volume might be great and absorption arrangements necessary.

6. Binding agents perform an important service in retaining the pesticide in order to complete its combustion.

7. Oxidizing agents perform an important service in lowering the temperatures required for completing combustion and in aiding oxidation.

8. Oxidizing agents appear unnecessary in the presence of binding agents.

9. Mineral oil is a satisfactory binding agent.

10. Polyethylene serves the same purpose as mineral oil in acting as a binding agent and serving as a combustible. It has the further advantage of serving as a suitable liner for most pesticide containers.

11. It is recommended that combustible pesticides be packaged in light polyethylene packs or lightweight polyethylene bags surrounded by a combustible container such as a corrugated package or fiber carton.

12. It is further recommended that future work be carried out in the following areas:

   a. The design of polyethylene containers for most efficient small-scale combustion (where heavy-wall polyethylene bags or containers are to be used, the use of pleated accordion type or jointed style to permit easy folding could involve a patentable concept)

   b. The use of other plastics

   c. In large-scale combustion, the presence of a large quantity of polymer may cause problems due to incomplete combustion, carbon formation, and gum formation. Work should be performed to investigate these possibilities

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and to develop solutions to such problems should they arise.

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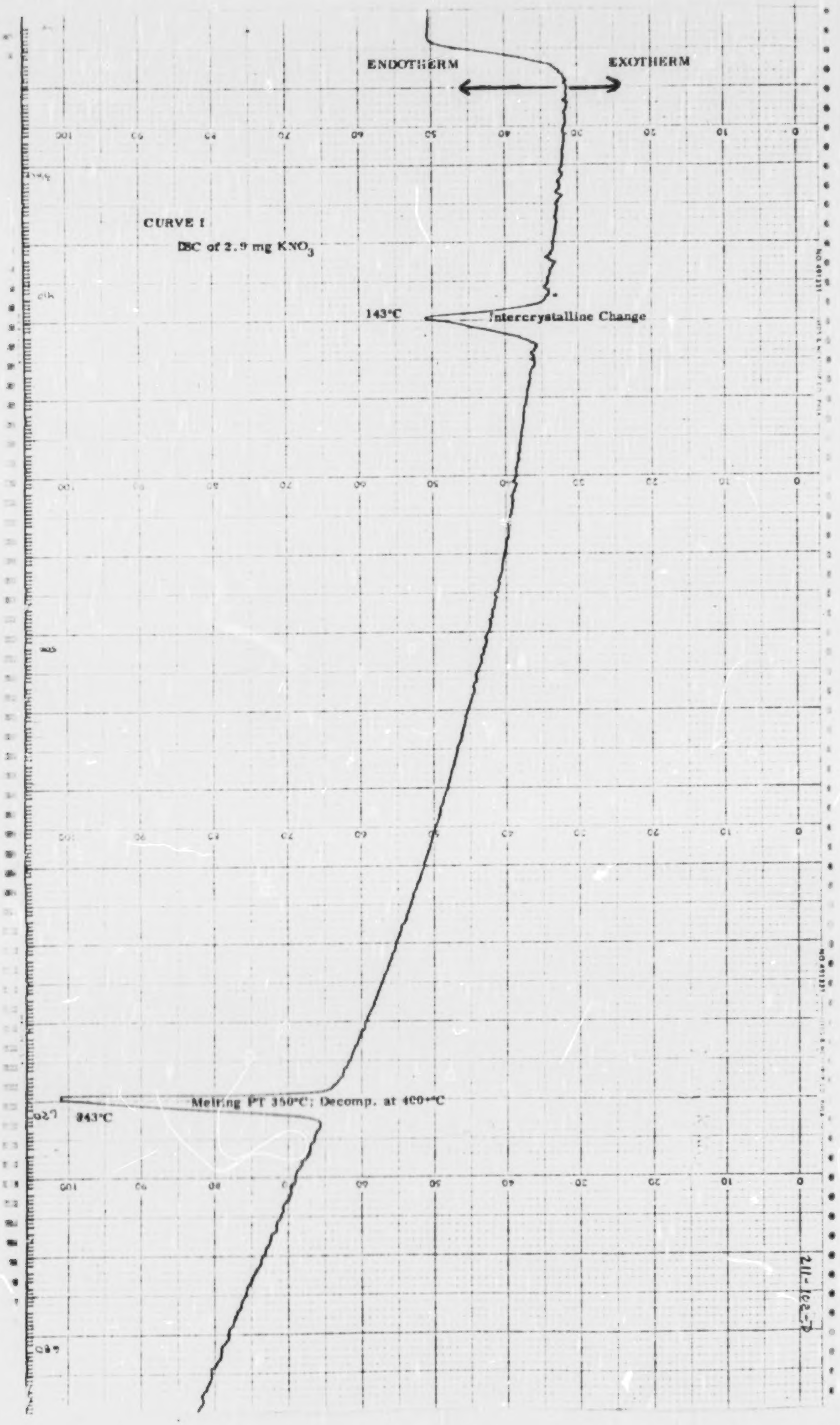
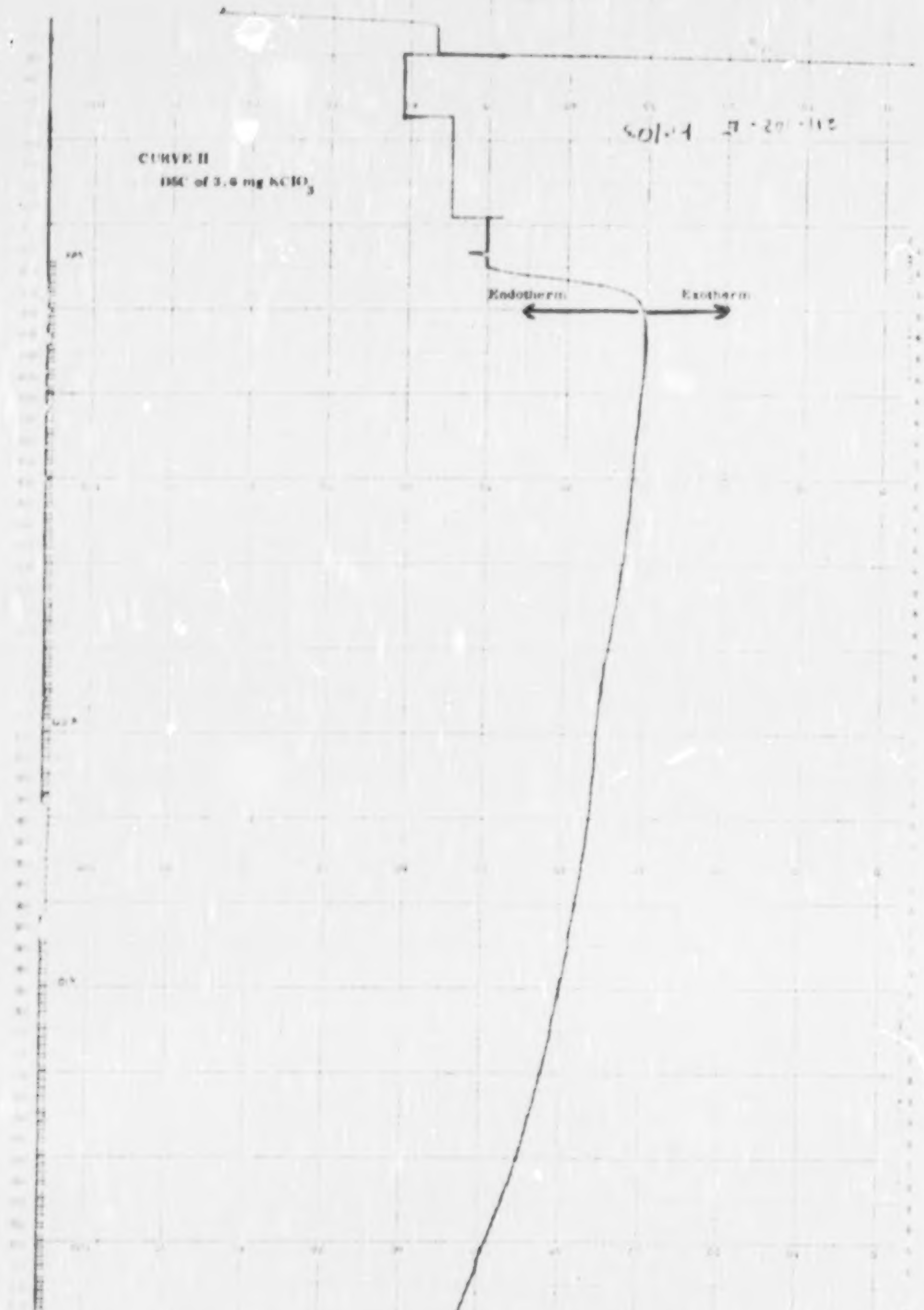
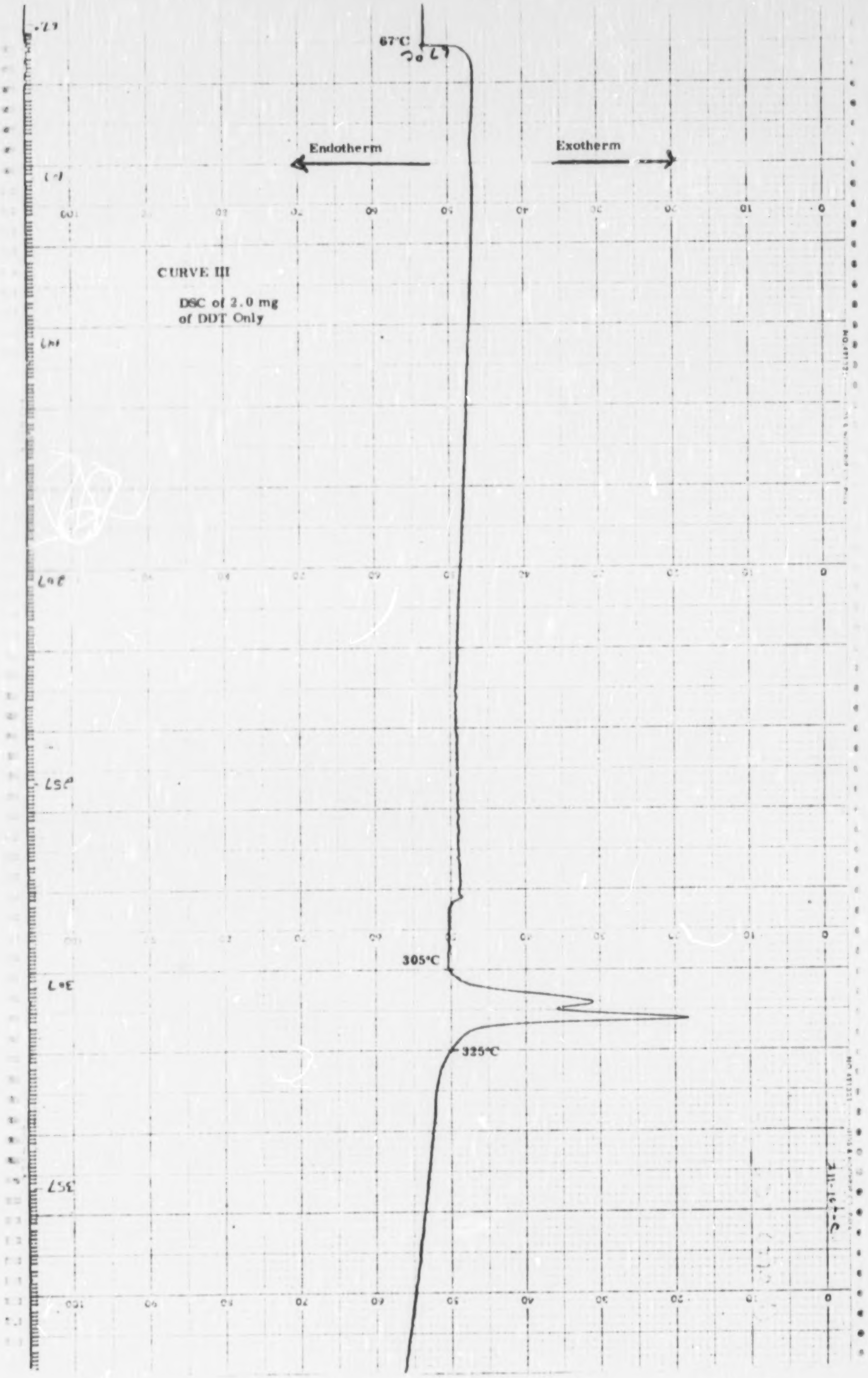
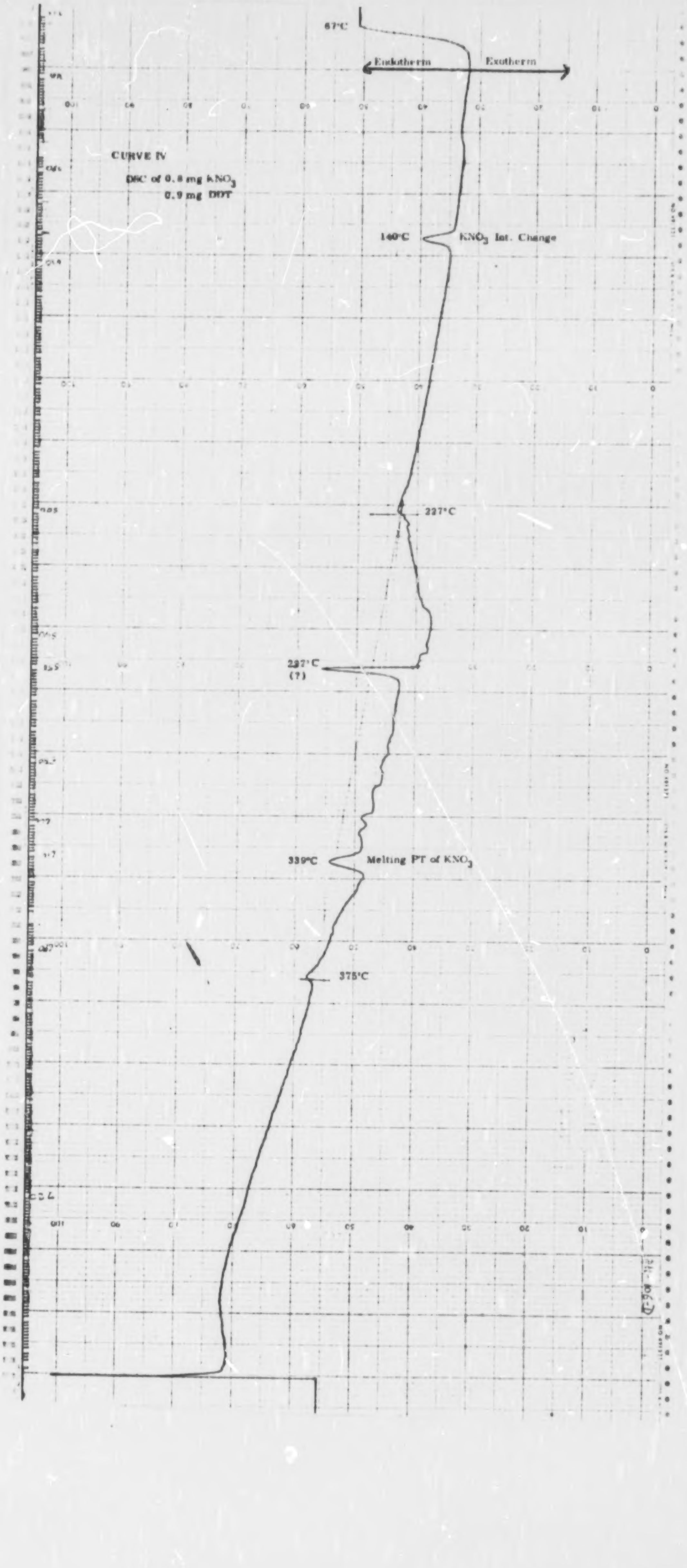

ENDOTHERM
EXOTHERM
CURVE I
DSC of 2.9 mg KNO_3
143°C
Intercrystalline Change
Melting PT 350°C; Decomp. at 400+°C
343°C
100
90
80
70
60
50
40
30
20
10
0

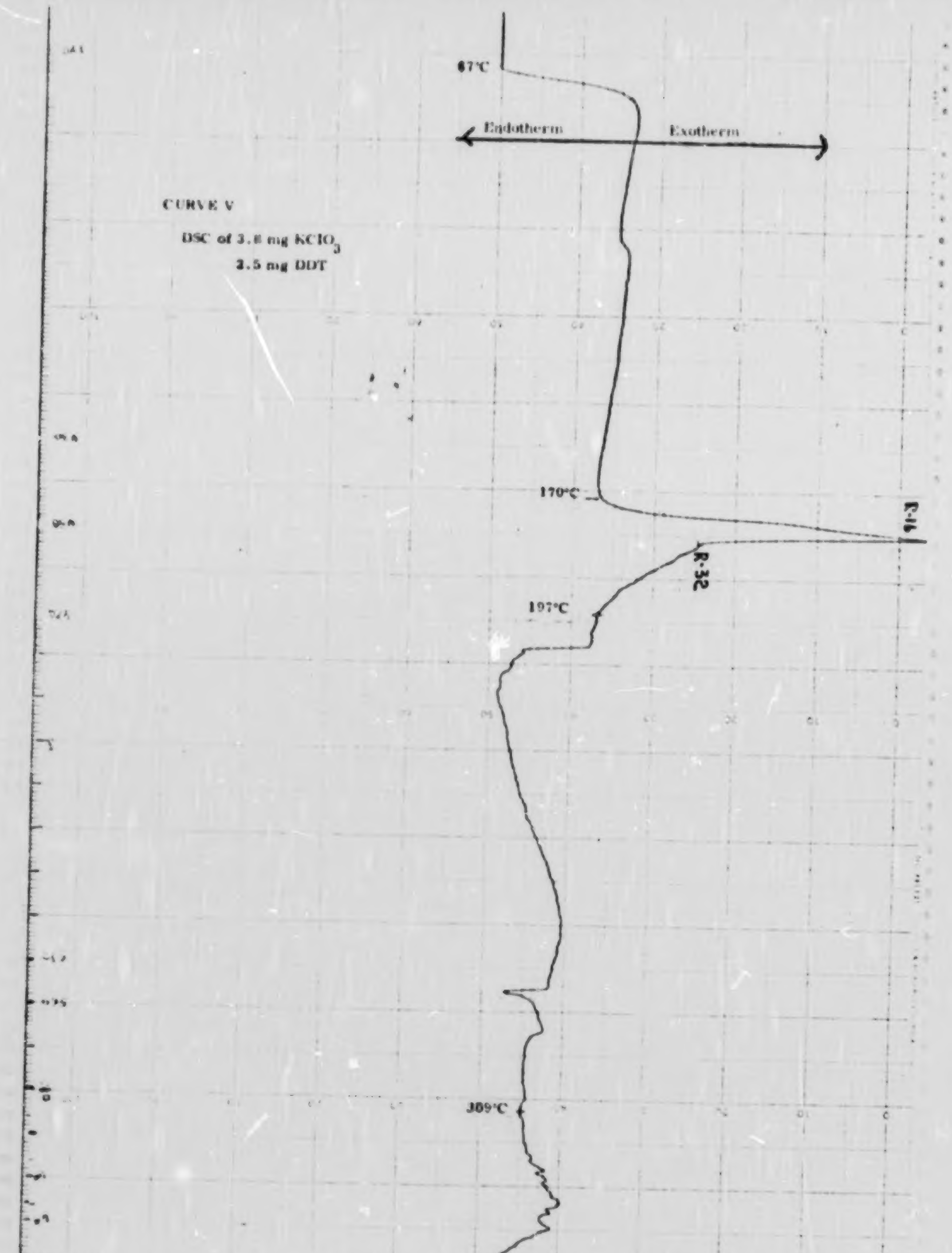

CURVE II
DSC of 3.6 mg $KClO_3$
B-201-112
Endotherm
Exotherm
28
370°C
24
Melting PT 368°C, Decomp. at 368°C
BLA
B-201-112



CURVE III

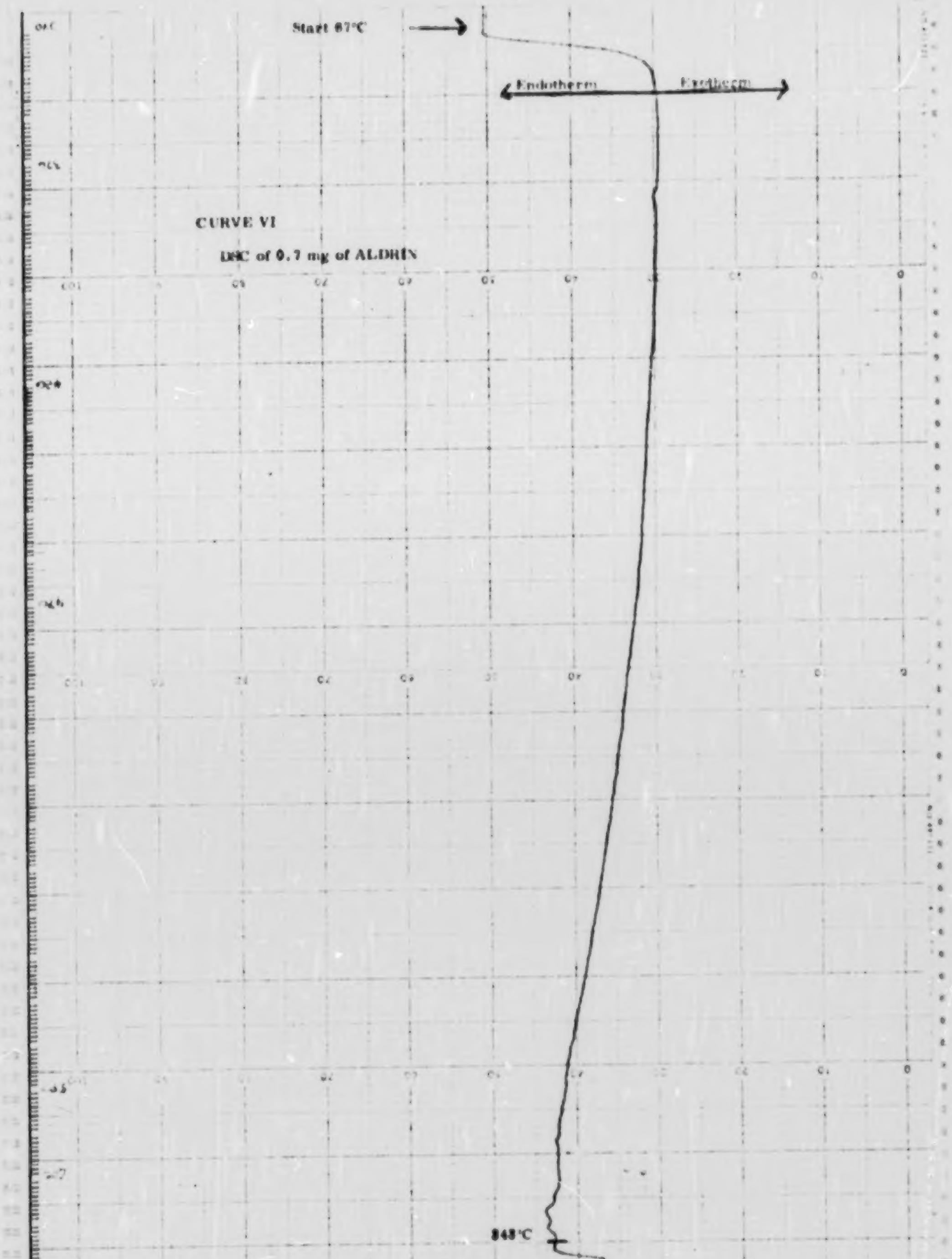
DSC of 2.0 mg of DDT Only


67°C
Endotherm
Exotherm
CURVE IV
DSC of 0.8 mg KNO3
0.9 mg DDT
140°C
KNO3 Int. Change
227°C
237°C
(?)
339°C
Melting PT of KNO3
375°C



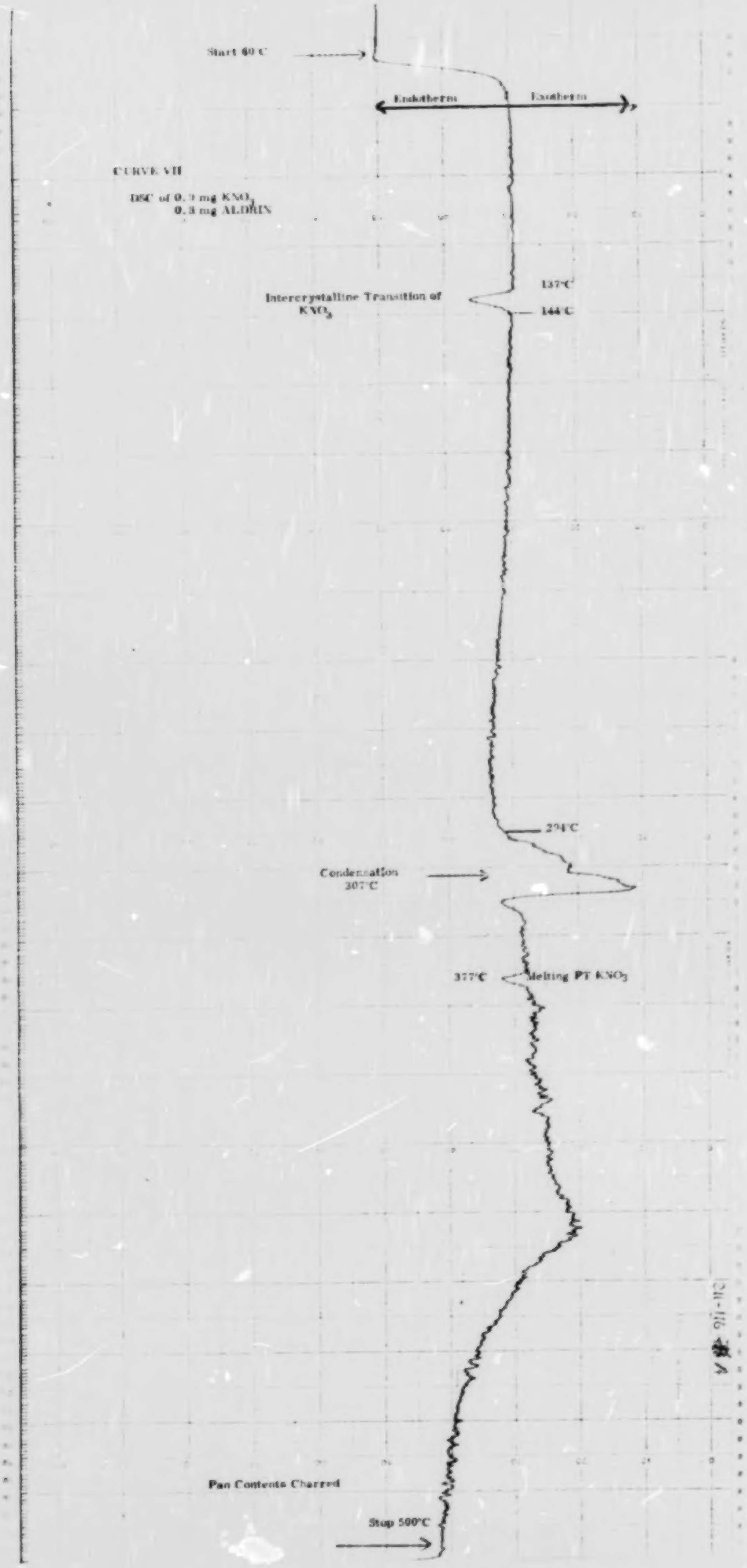
CURVE V

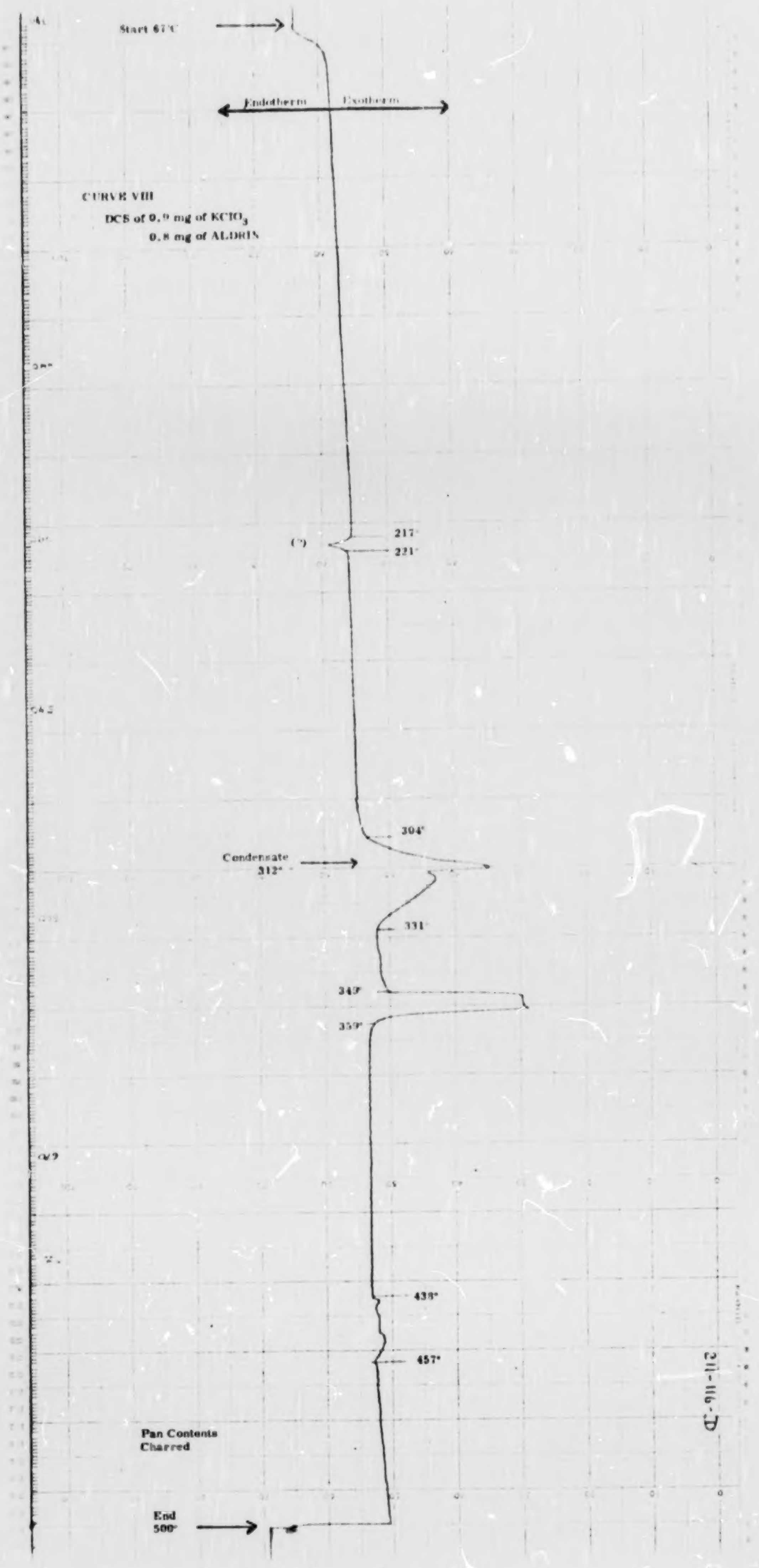
DSC of 3.8 mg $KClO_3$
3.5 mg DDT



CURVE VI

DSC of 0.7 mg of ALDRIN

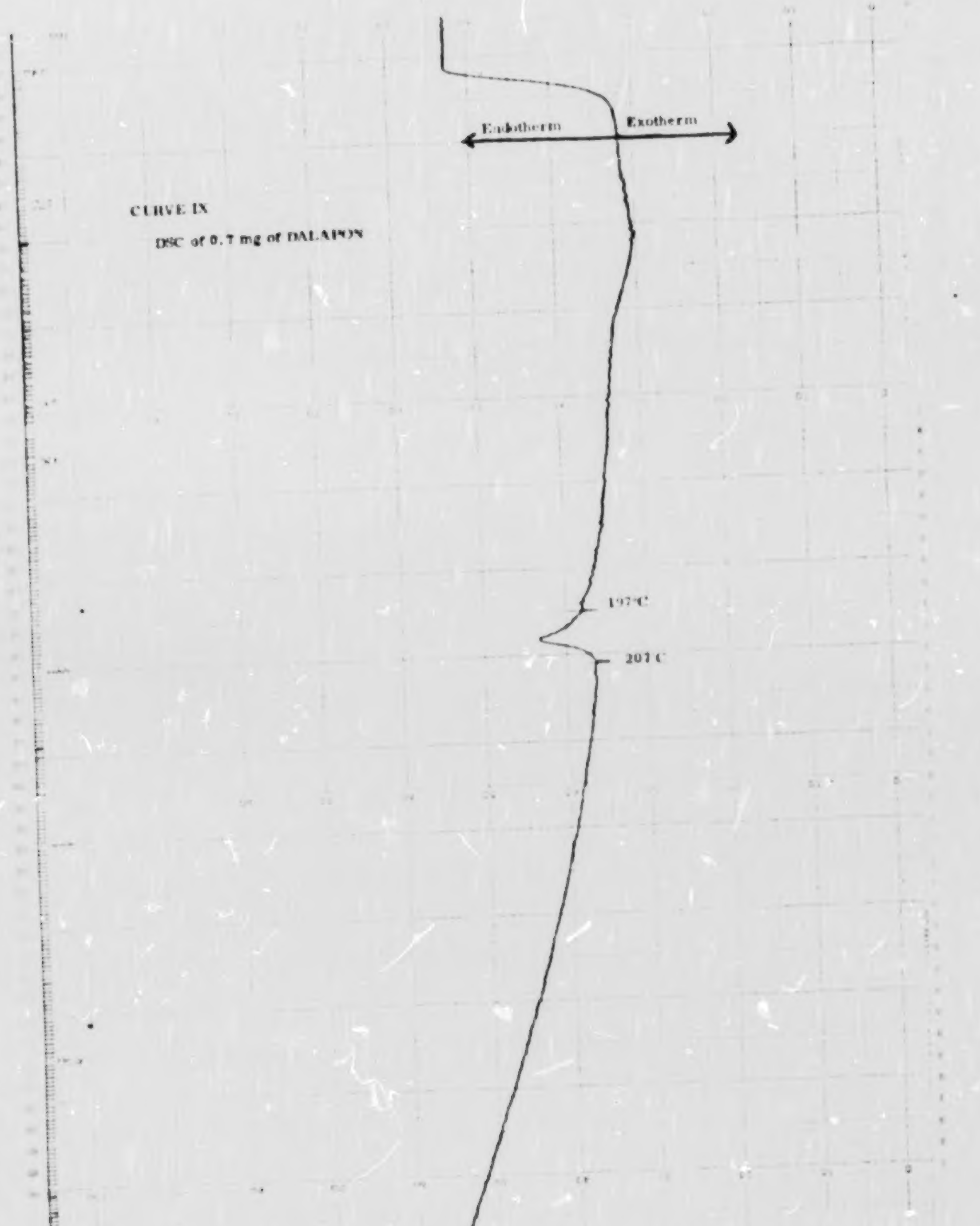

Start 60°C
Endotherm
Exotherm
CURVE VII
DSC of 0.9 mg KNO$_3$
0.3 mg ALDRIN
137°C
Intercrystalline Transition of KNO$_3$
144°C
294°C
Condensation 307°C
377°C
Melting PT KNO$_3$
Pan Contents Charred
Stop 500°C



CURVE VIII

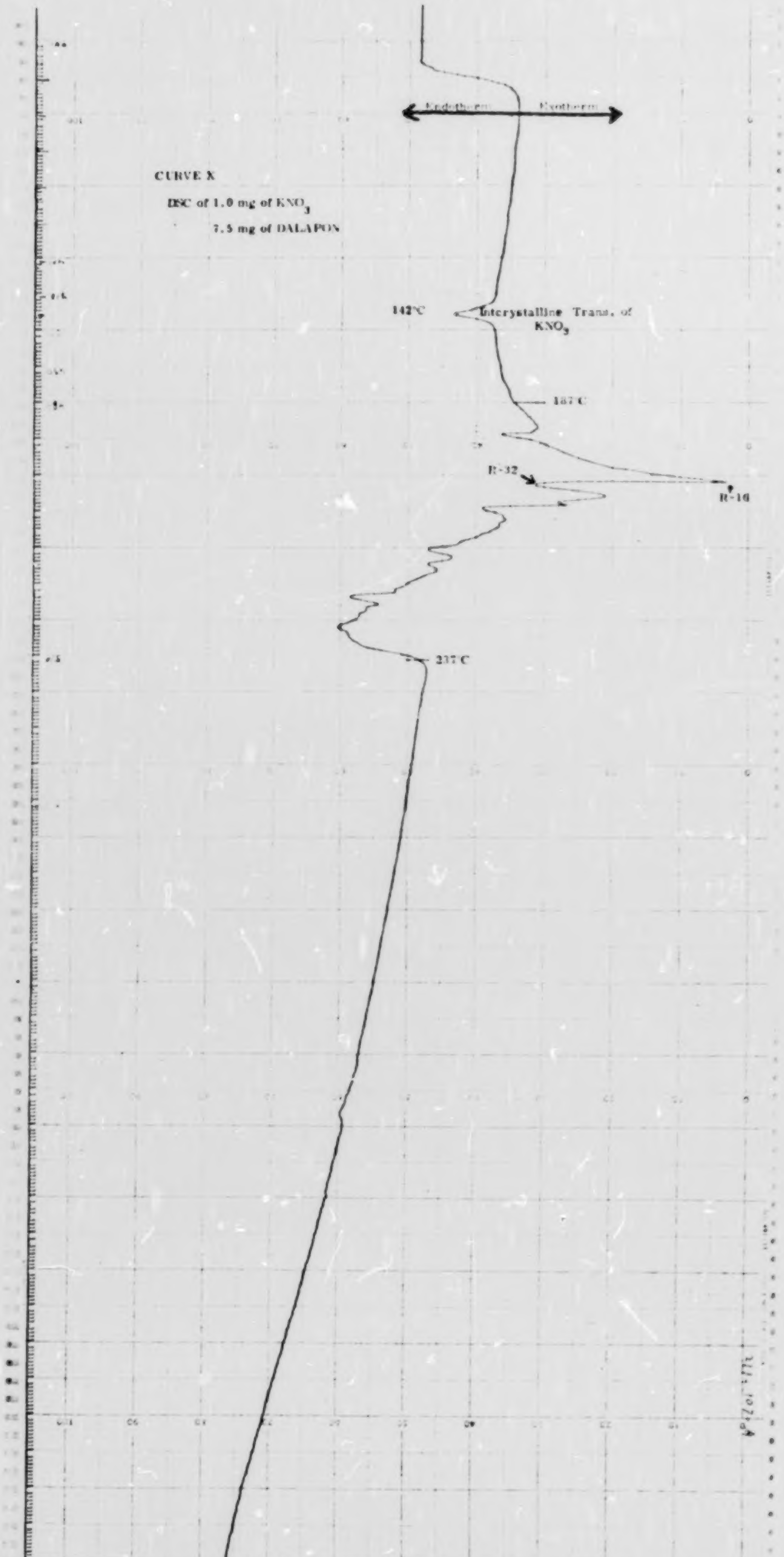
DCS of 0.9 mg of $KClO_3$

0.8 mg of ALDRIN



CURVE IX

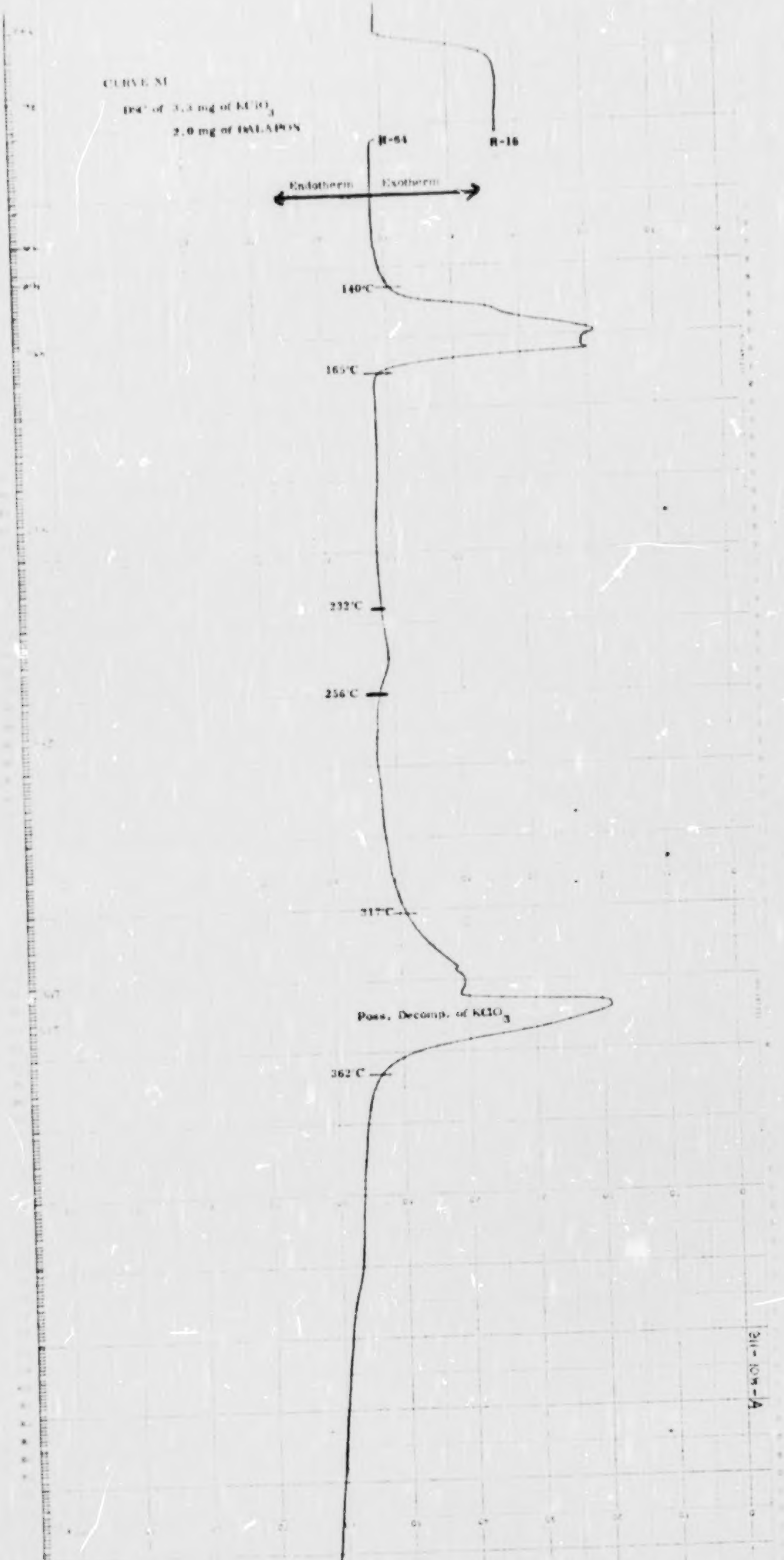
DSC of 0.7 mg of DALAPON

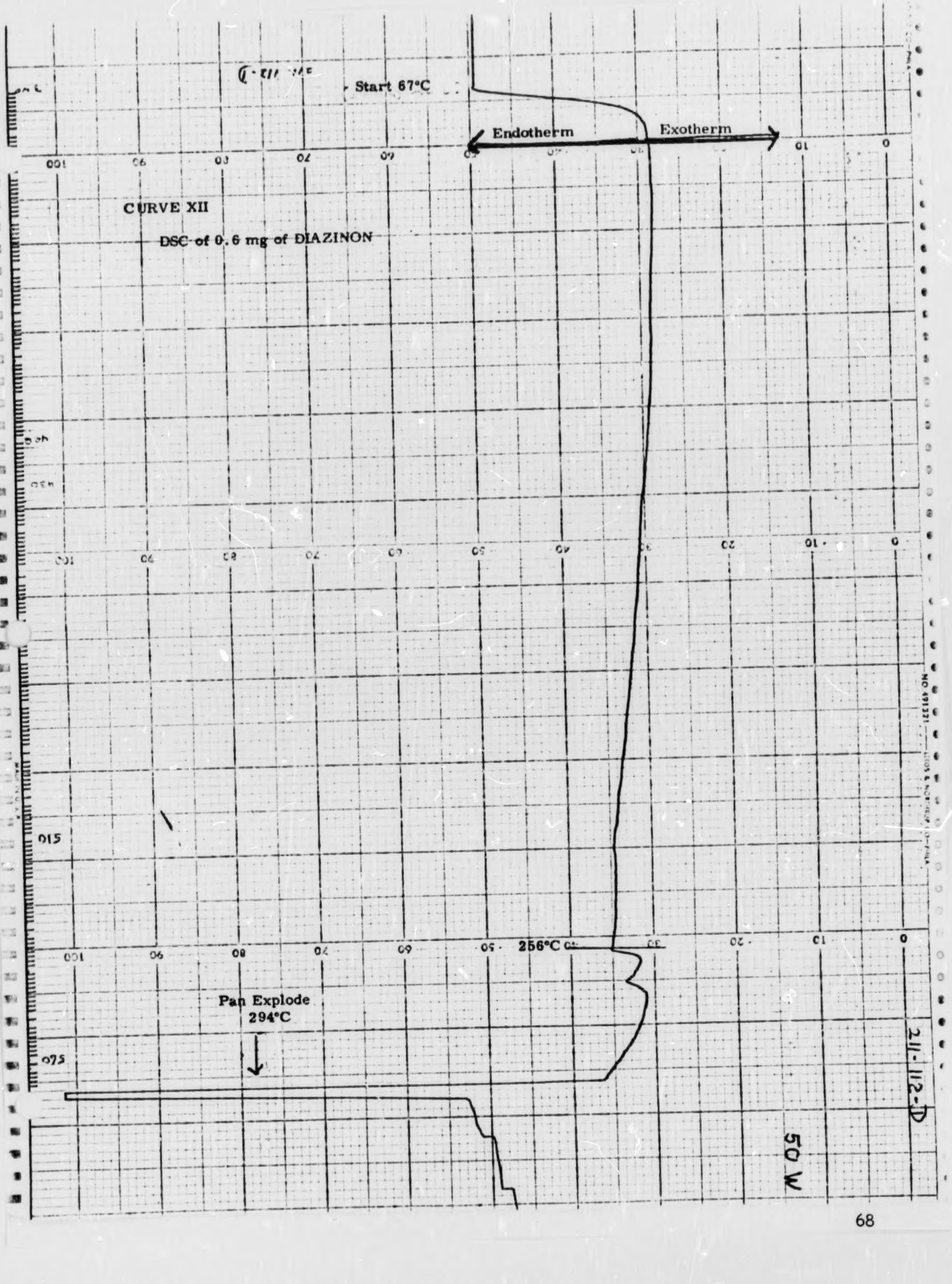


CURVE X

DSC of 1.0 mg of KNO_3

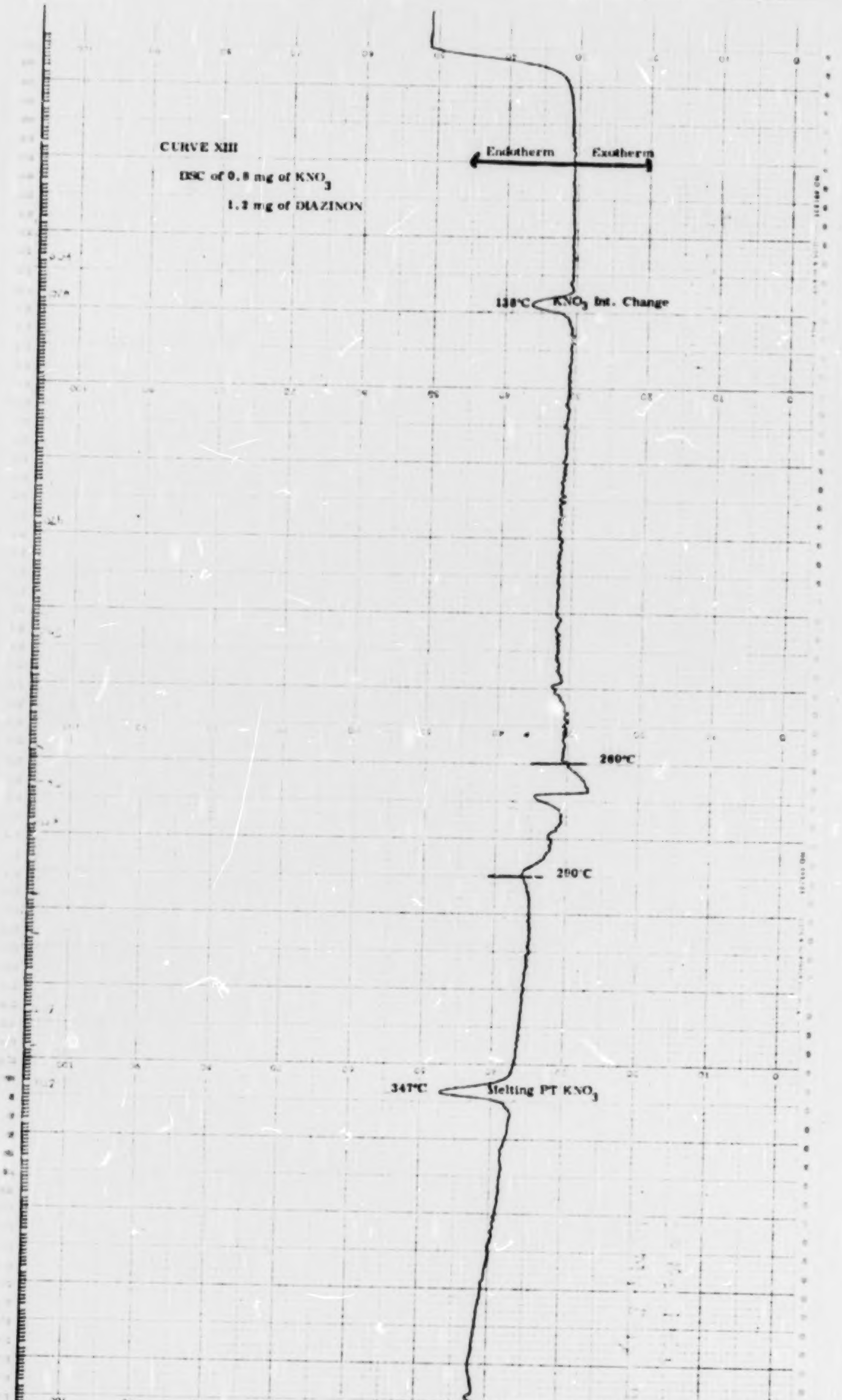
7.5 mg of DALAPON


CURVE XI
DTA of 3.3 mg of KClO$_3$
2.0 mg of DALAPON
R-64
R-16
Endotherm
Exotherm
140°C
165°C
232°C
256°C
317°C
Poss. Decomp. of KClO$_3$
362°C



CURVE XII

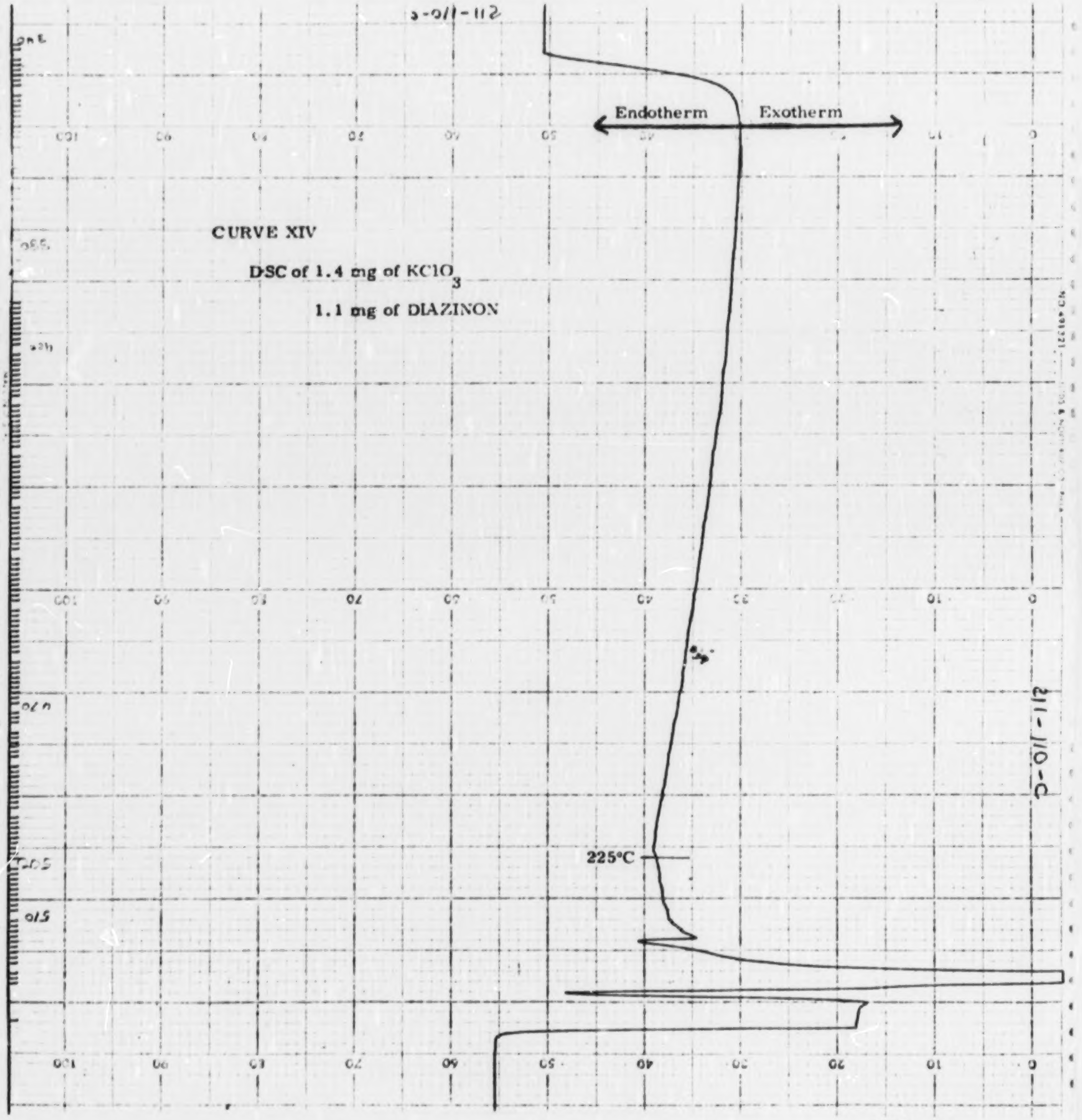
DSC of 0.6 mg of DIAZINON



CURVE XIII

DSC of 0.8 mg of KNO_3

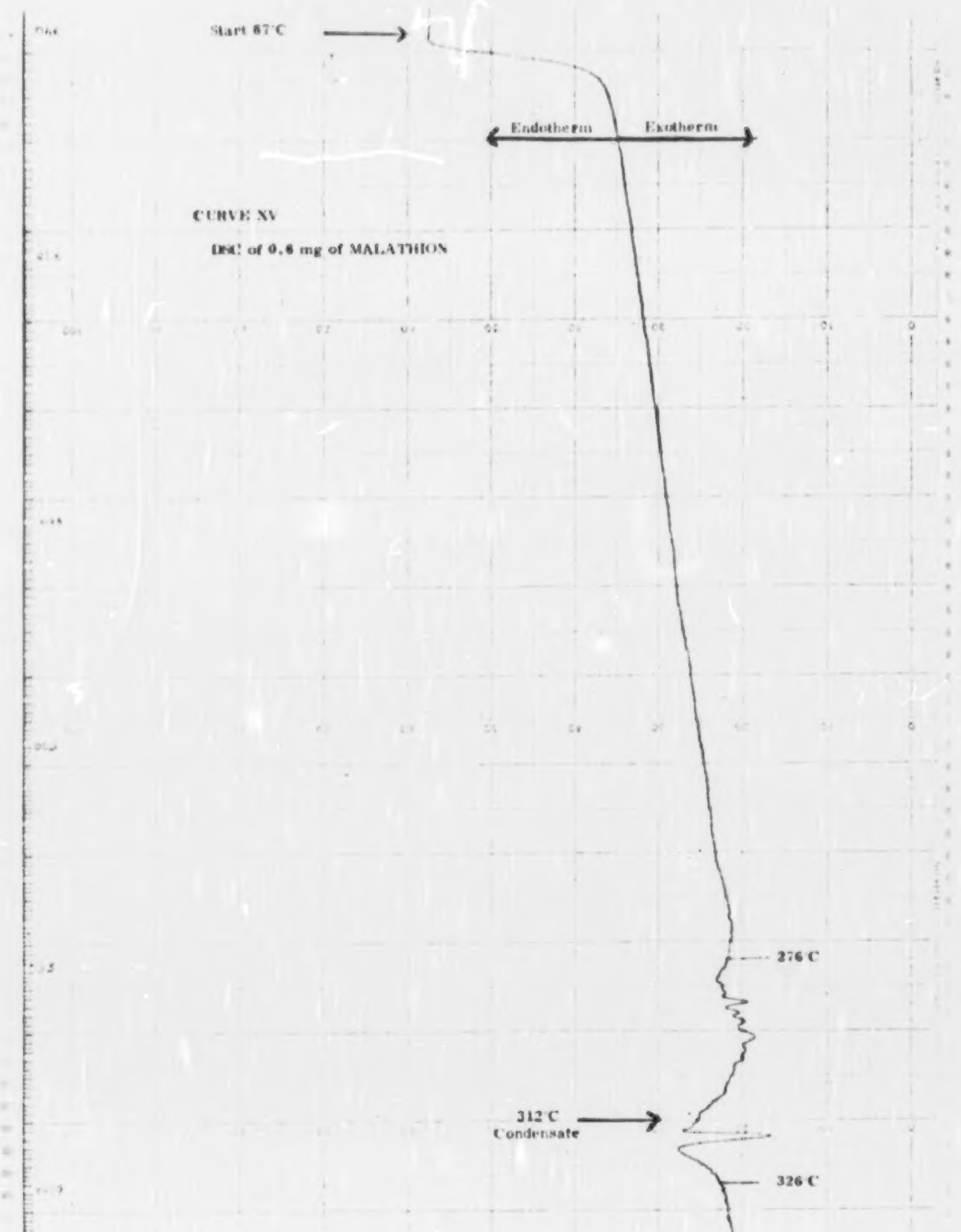
1.2 mg of DIAZINON

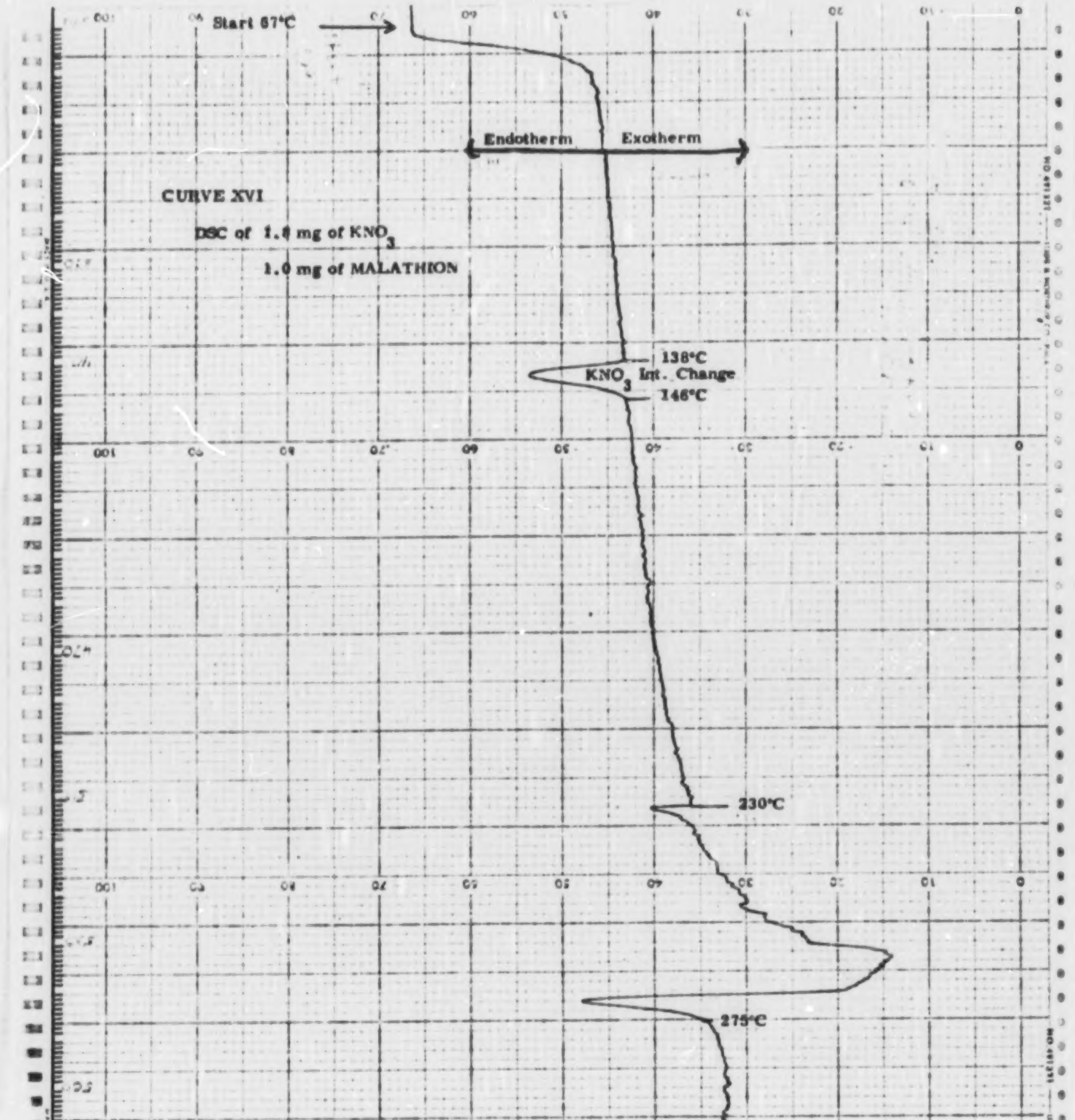


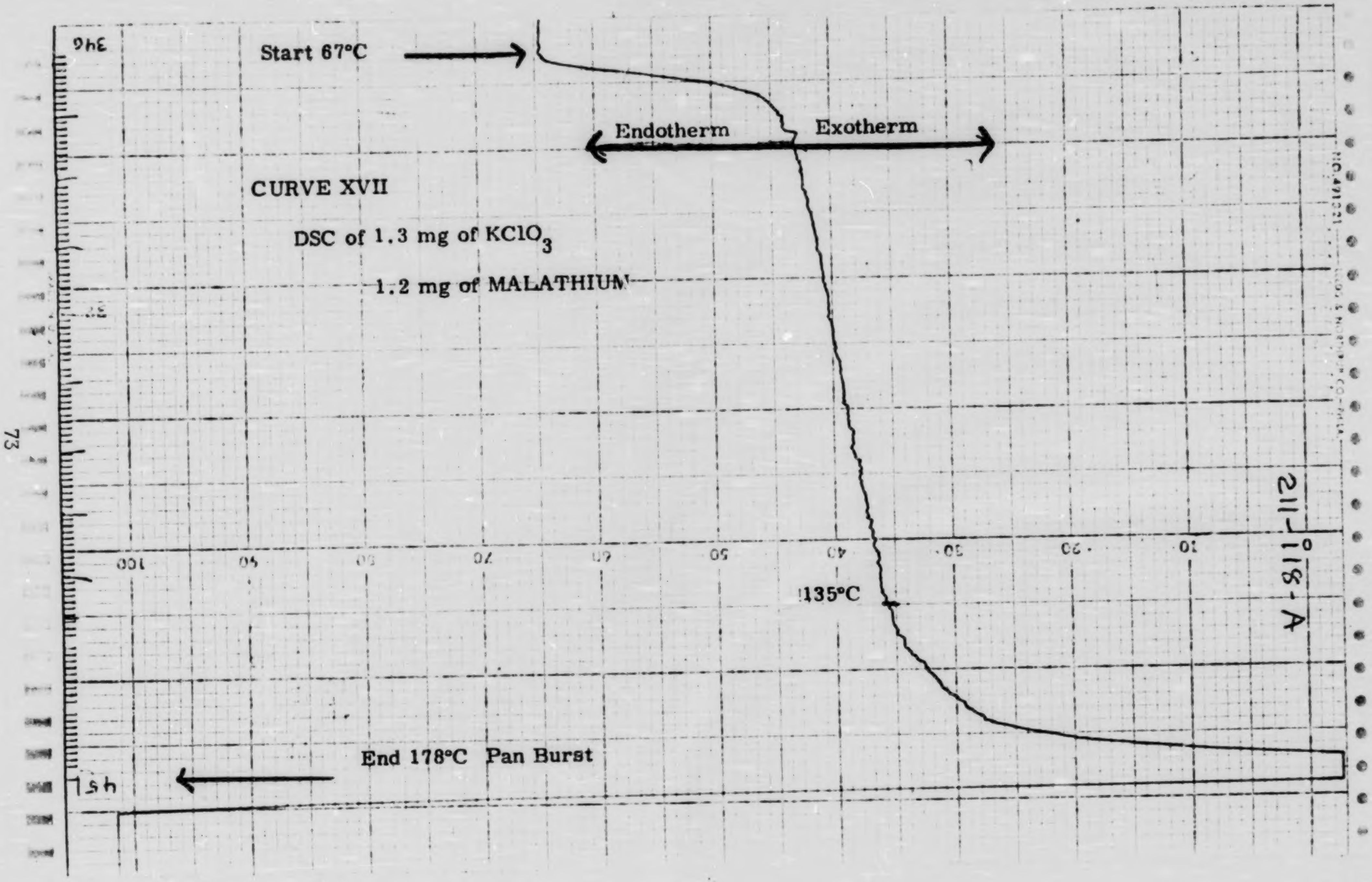
CURVE XIV

DSC of 1.4 mg of $KClO_3$

1.1 mg of DIAZINON


Start 87°C
Endotherm
Exotherm
CURVE XV
DSC of 0.6 mg of MALATHION
276°C
312°C
Condensate
326°C
End 500°C
211-117-A


Start 67°C
Endotherm
Exotherm
CURVE XVI
DSC of 1.0 mg of KNO_3
1.0 mg of MALATHION
138°C
KNO_3 Int. Change
146°C
230°C
275°C
End
437°C
100
90
80
70
60
50
40
30
20
10
0
211-117-D



CURVE XVII

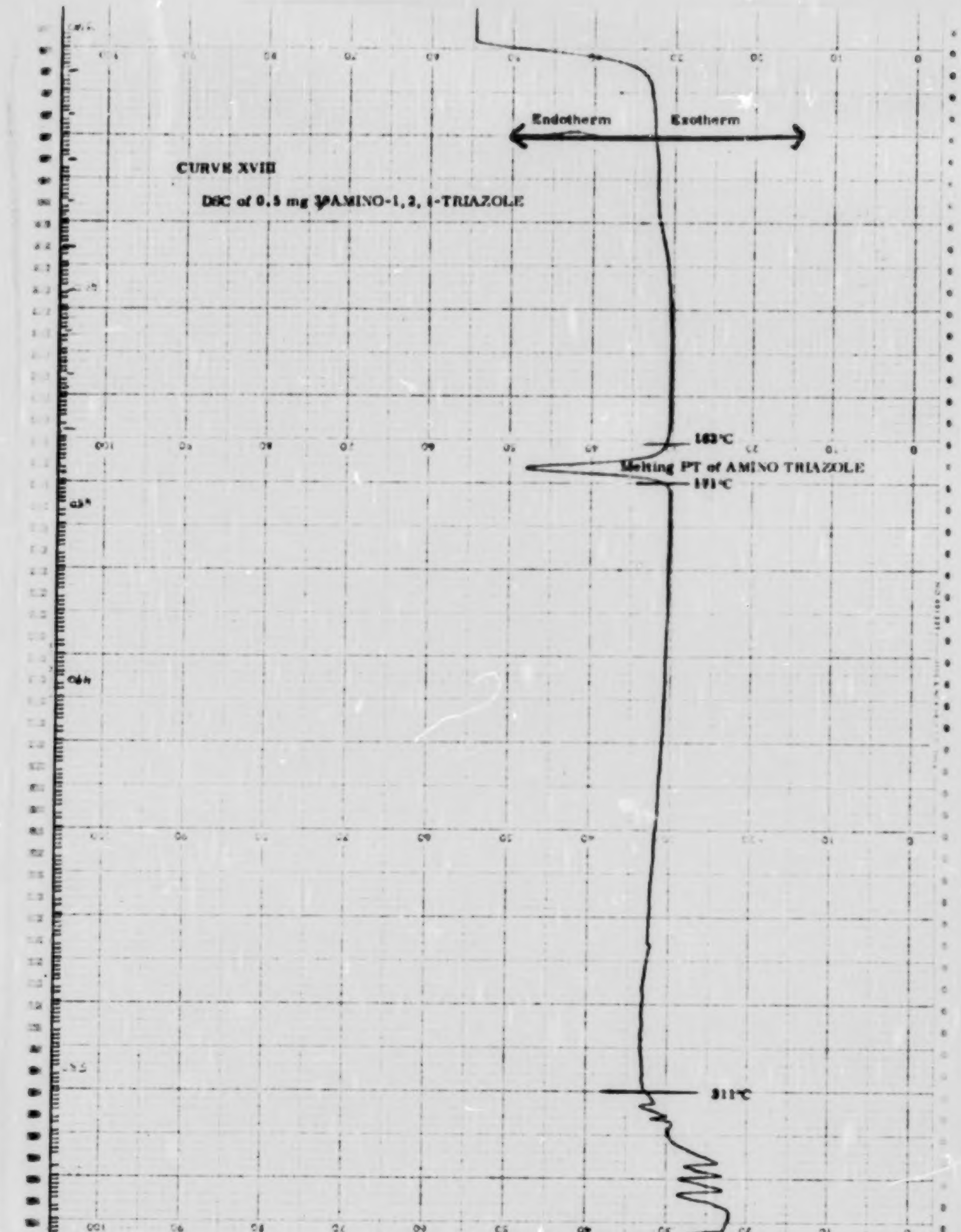
DSC of 1.3 mg of $KClO_3$

1.2 mg of MALATHIUM

Start 67°C

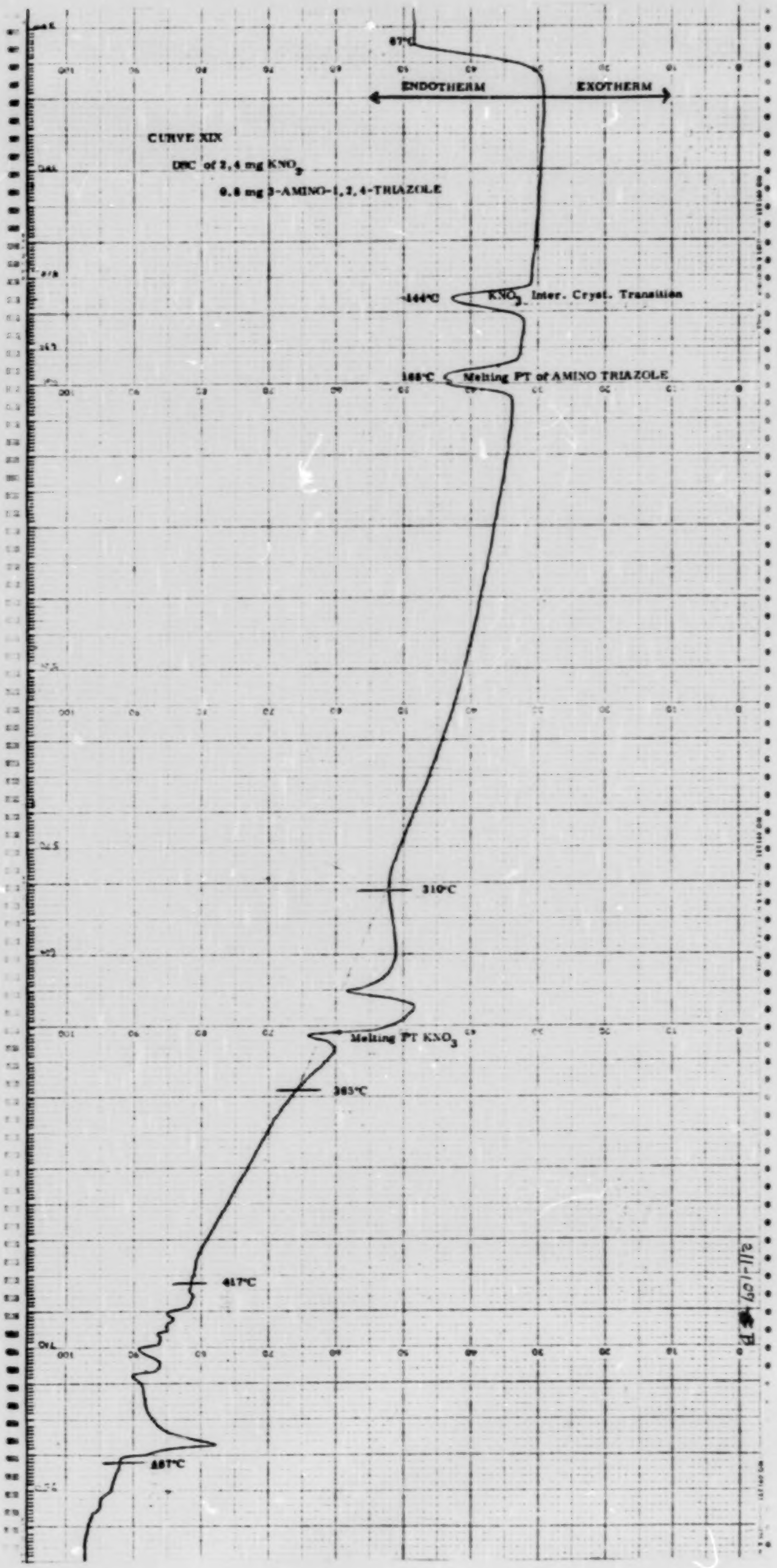
135°C

End 178°C Pan Burst



CURVE XVIII

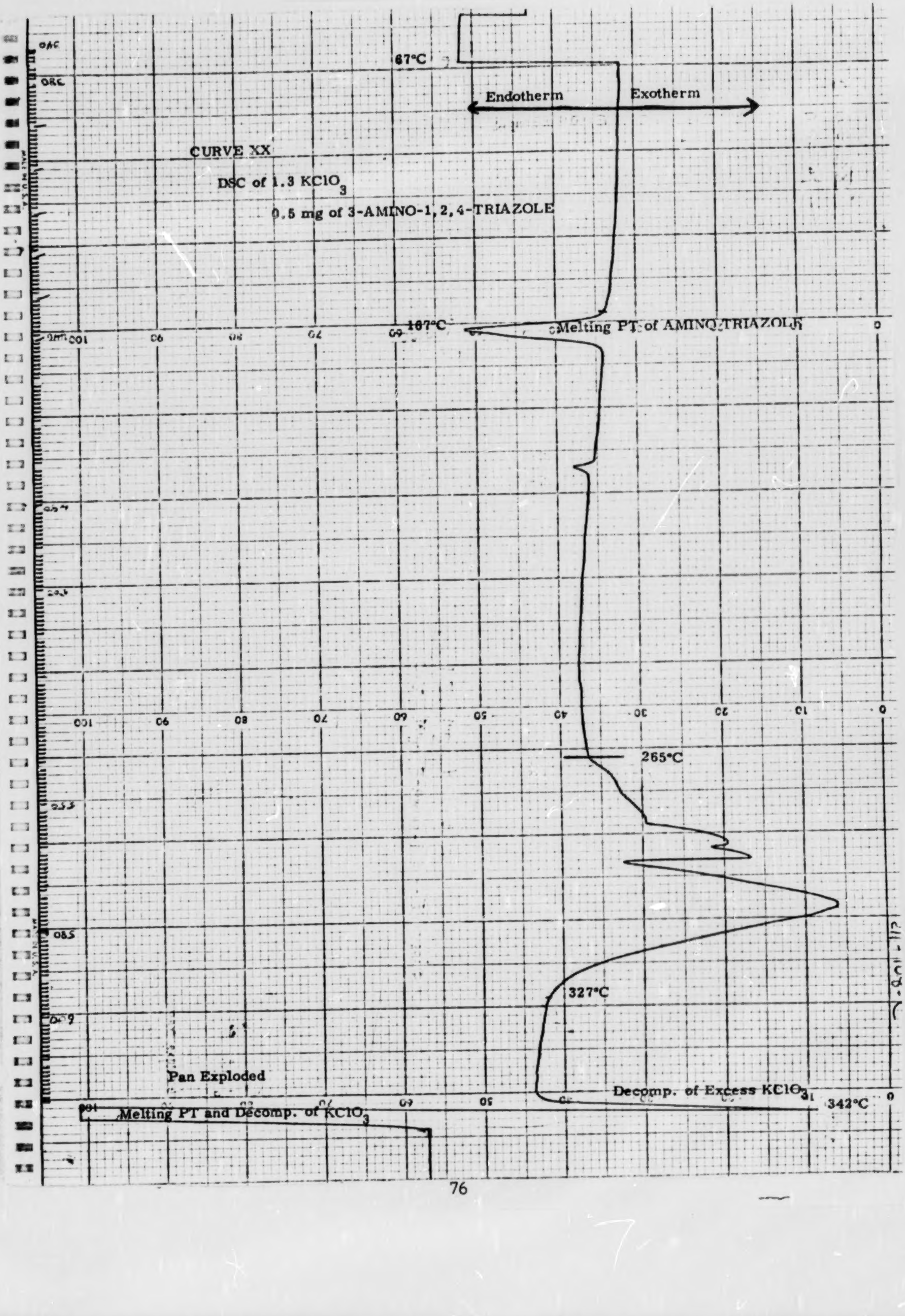
DSC of 0.5 mg 3-AMINO-1, 2, 4-TRIAZOLE



CURVE XIX

DSC of 2,4 mg KNO_3

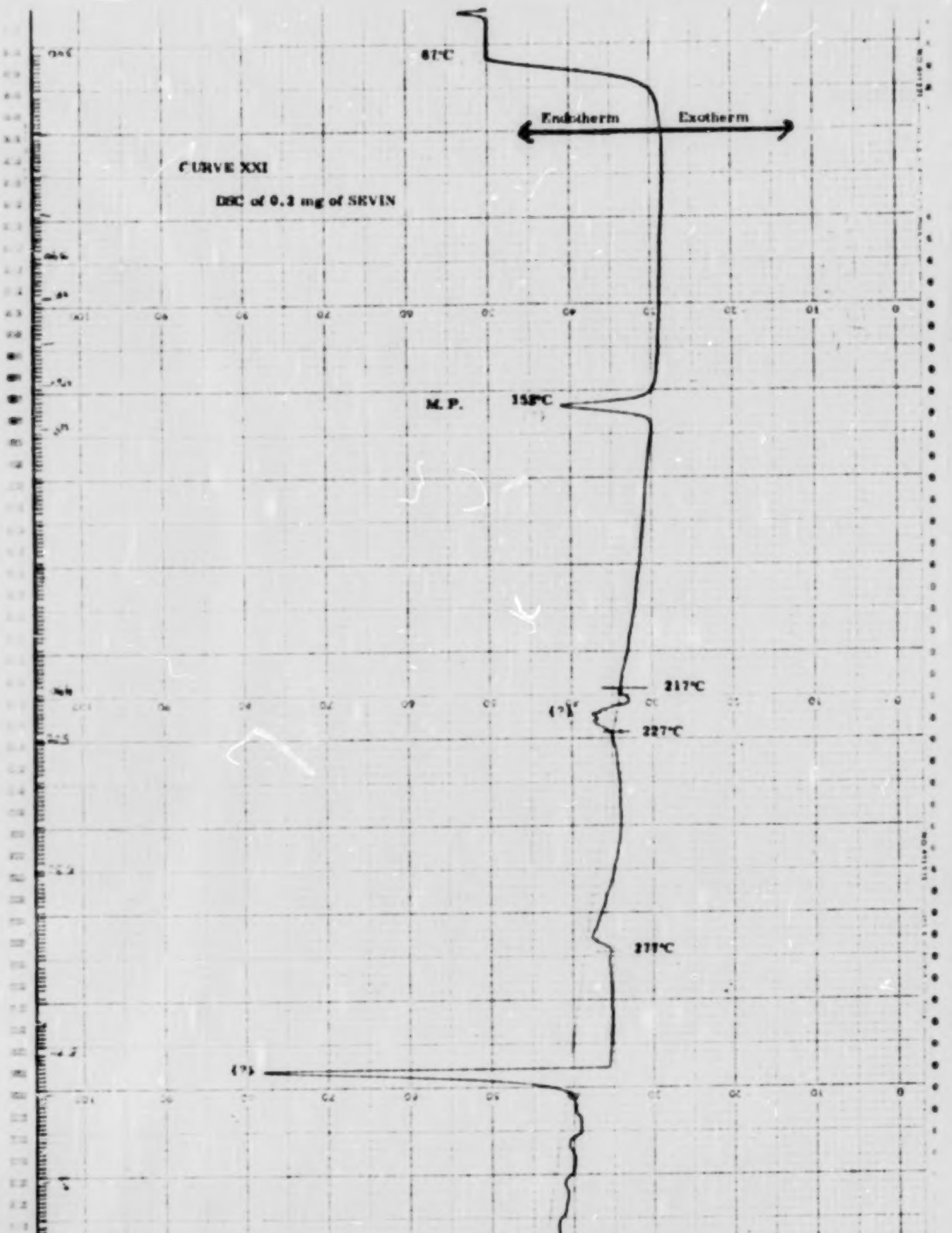
0.8 mg 3-AMINO-1,2,4-TRIAZOLE



CURVE XX

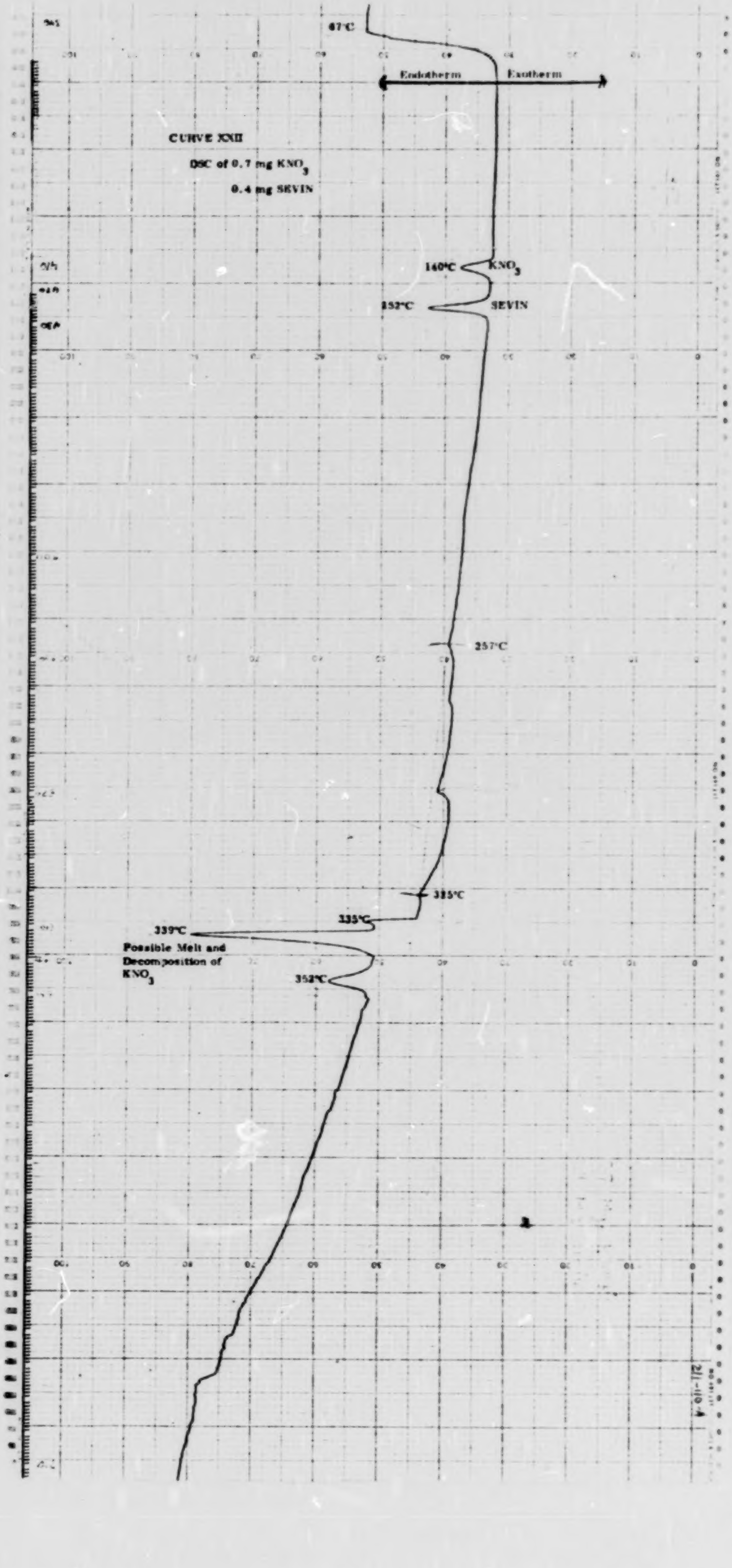
DSC of 1.3 $KClO_3$

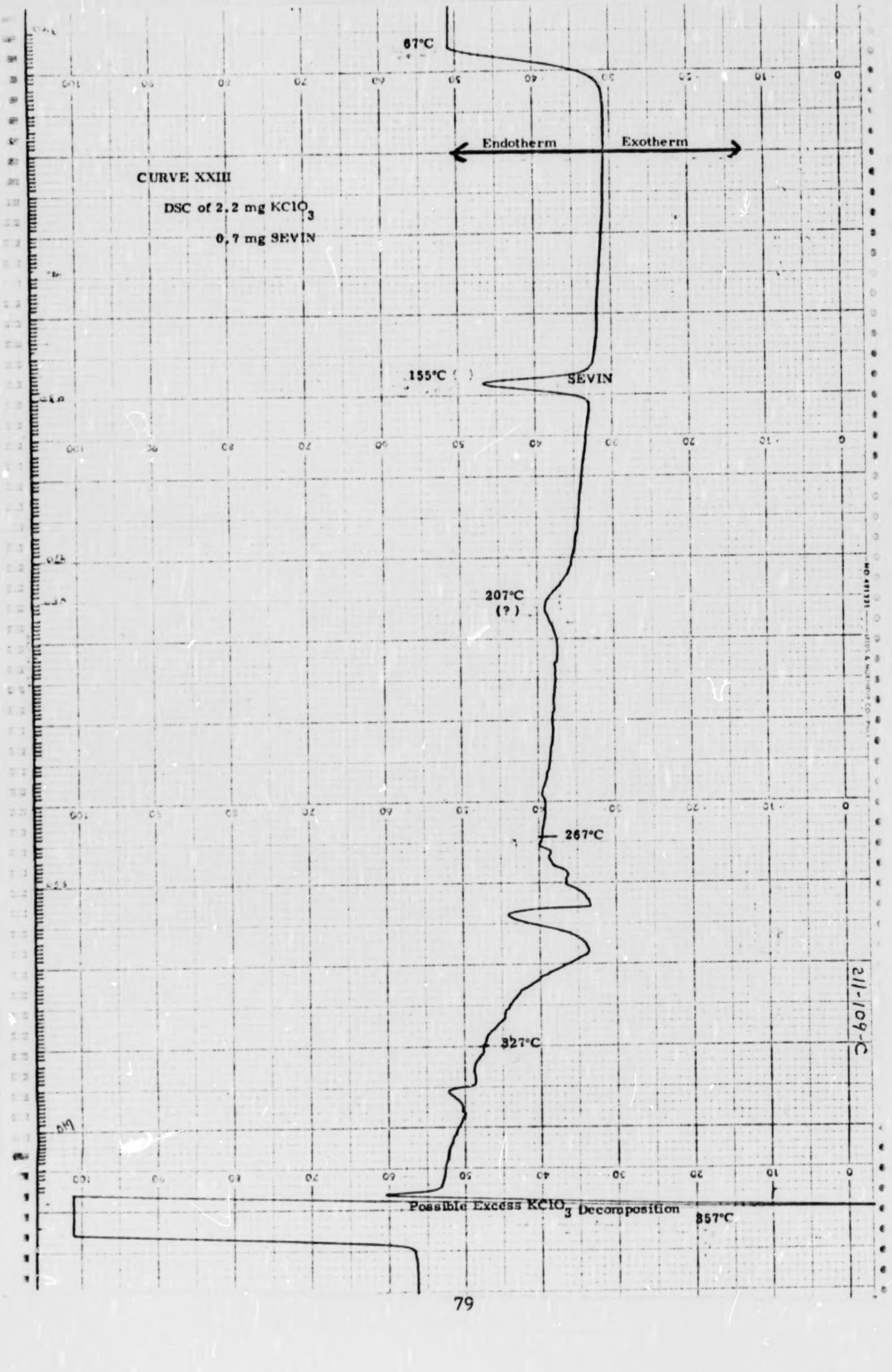
0.5 mg of 3-AMINO-1,2,4-TRIAZOLE



CURVE XXI

DSC of 0.2 mg of SEVIN

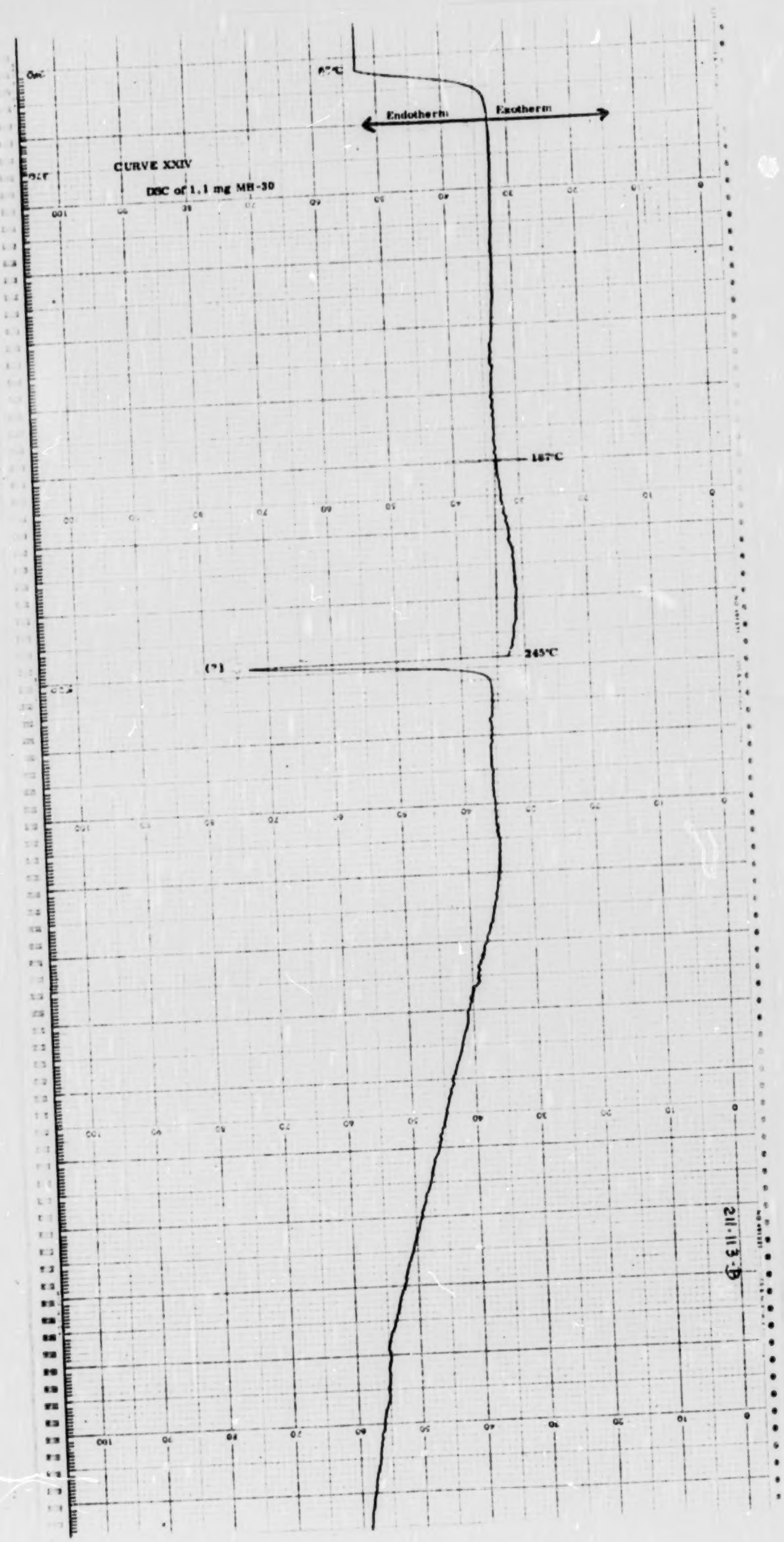

67°C
Endotherm
Exotherm
CURVE XXII
DSC of 0.7 mg KNO_3
0.4 mg SEVIN
140°C
KNO_3
152°C
SEVIN
257°C
325°C
335°C
339°C
Possible Melt and Decomposition of KNO_3
352°C



CURVE XXIII

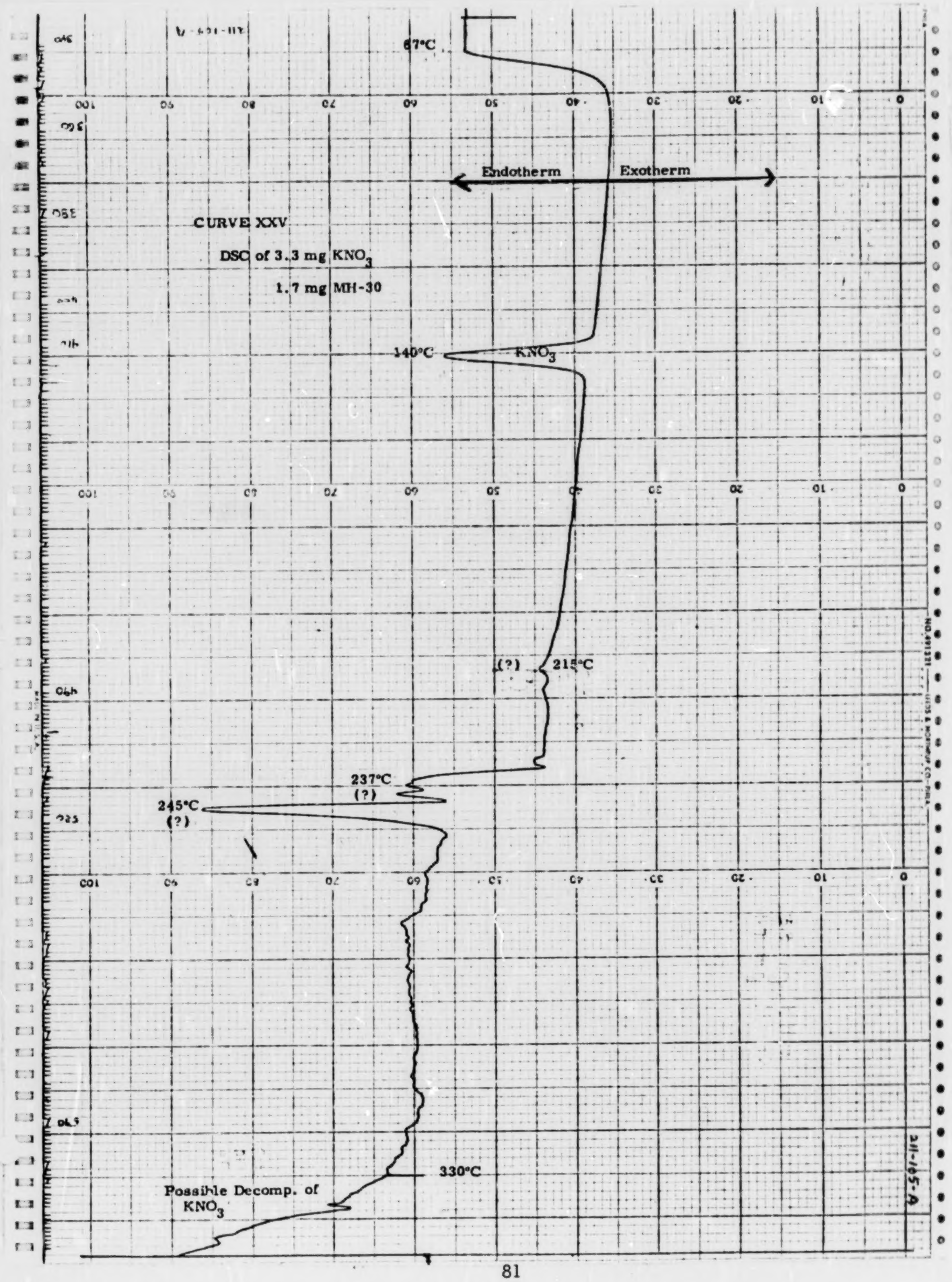
DSC of 2.2 mg $KClO_3$

0.7 mg SEVIN



CURVE XXIV

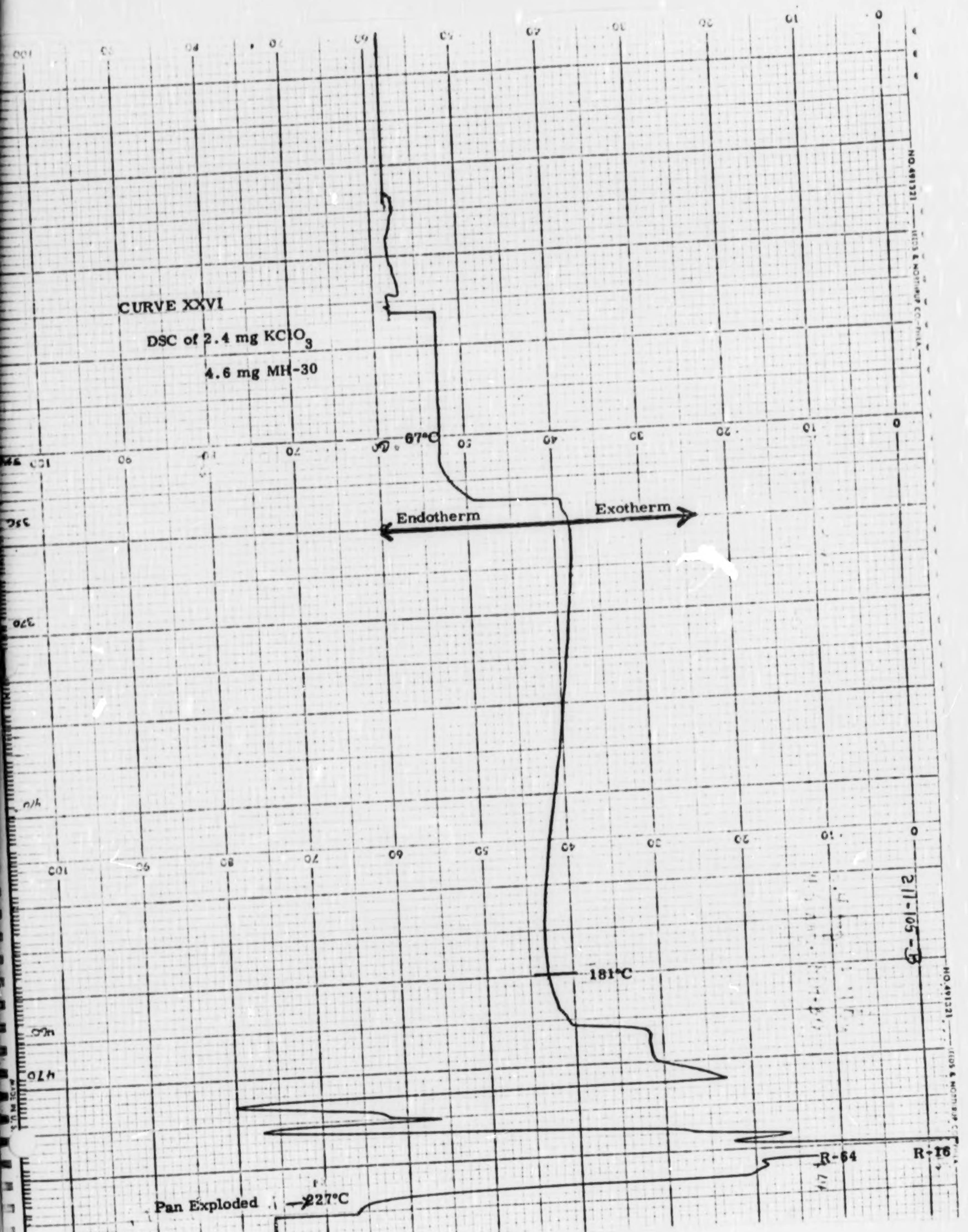
DSC of 1.1 mg MH-30



CURVE XXV

DSC of 3.3 mg KNO_3

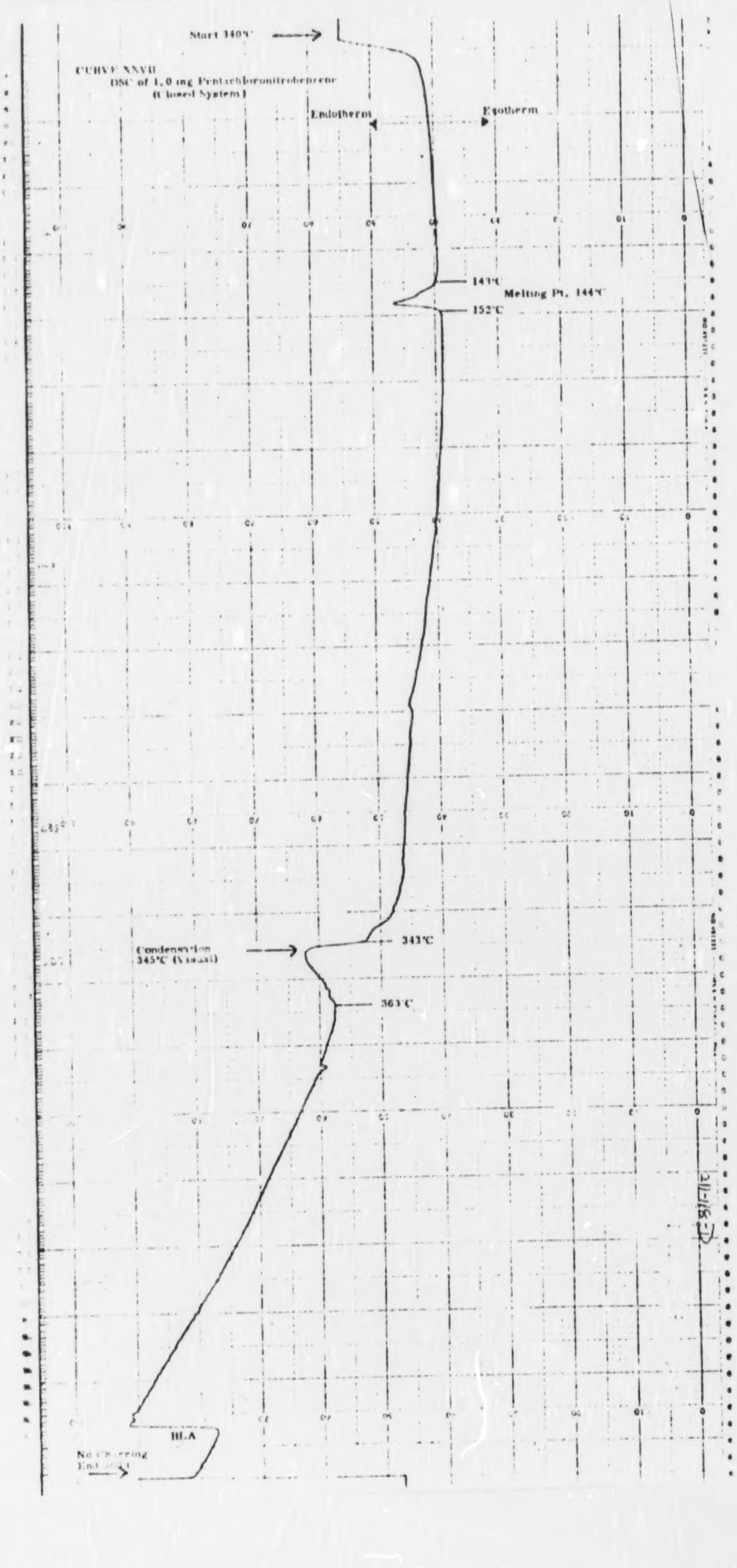
1.7 mg MH-30



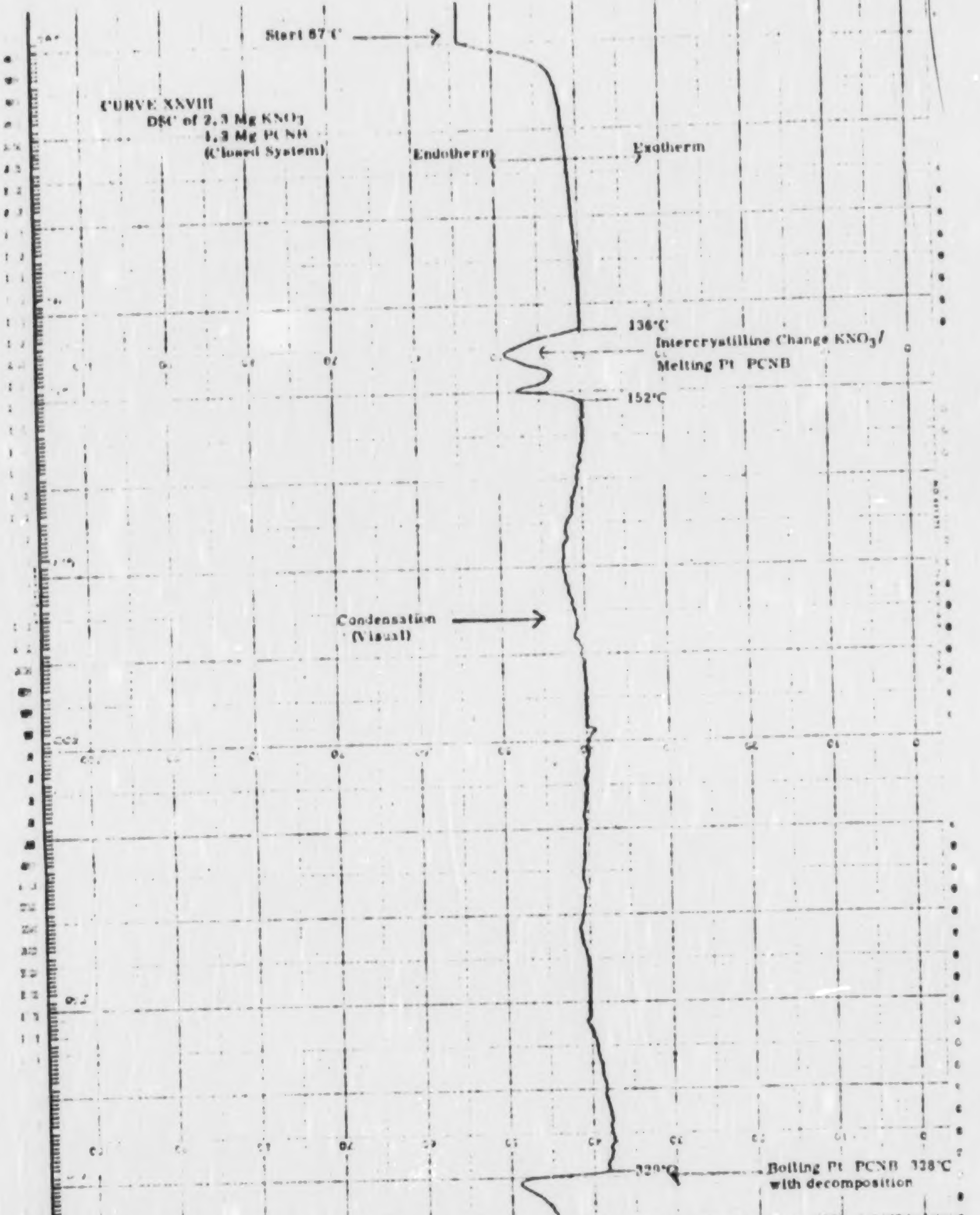
CURVE XXVI

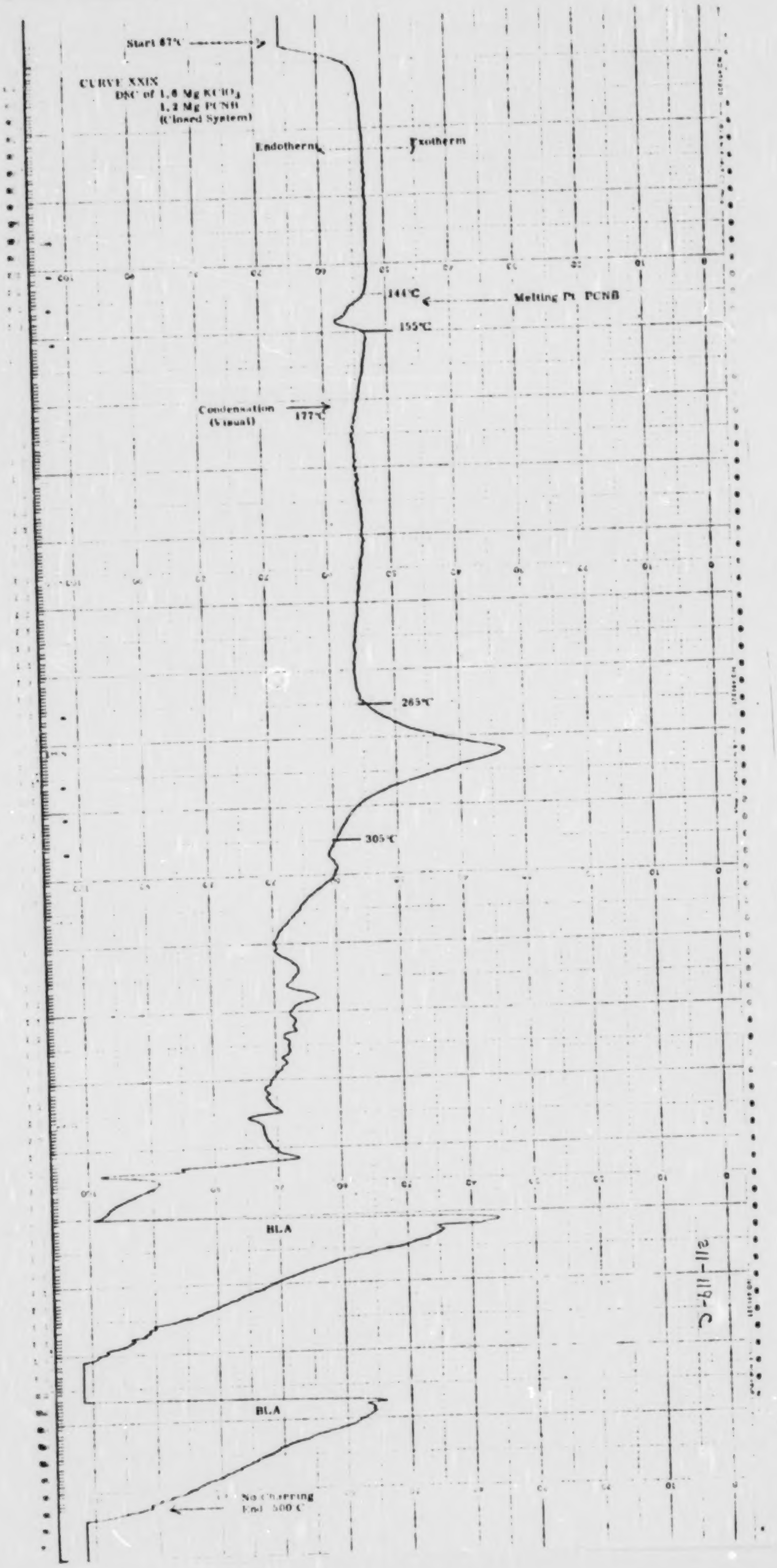
DSC of 2.4 mg $KClO_3$

4.6 mg MH-30

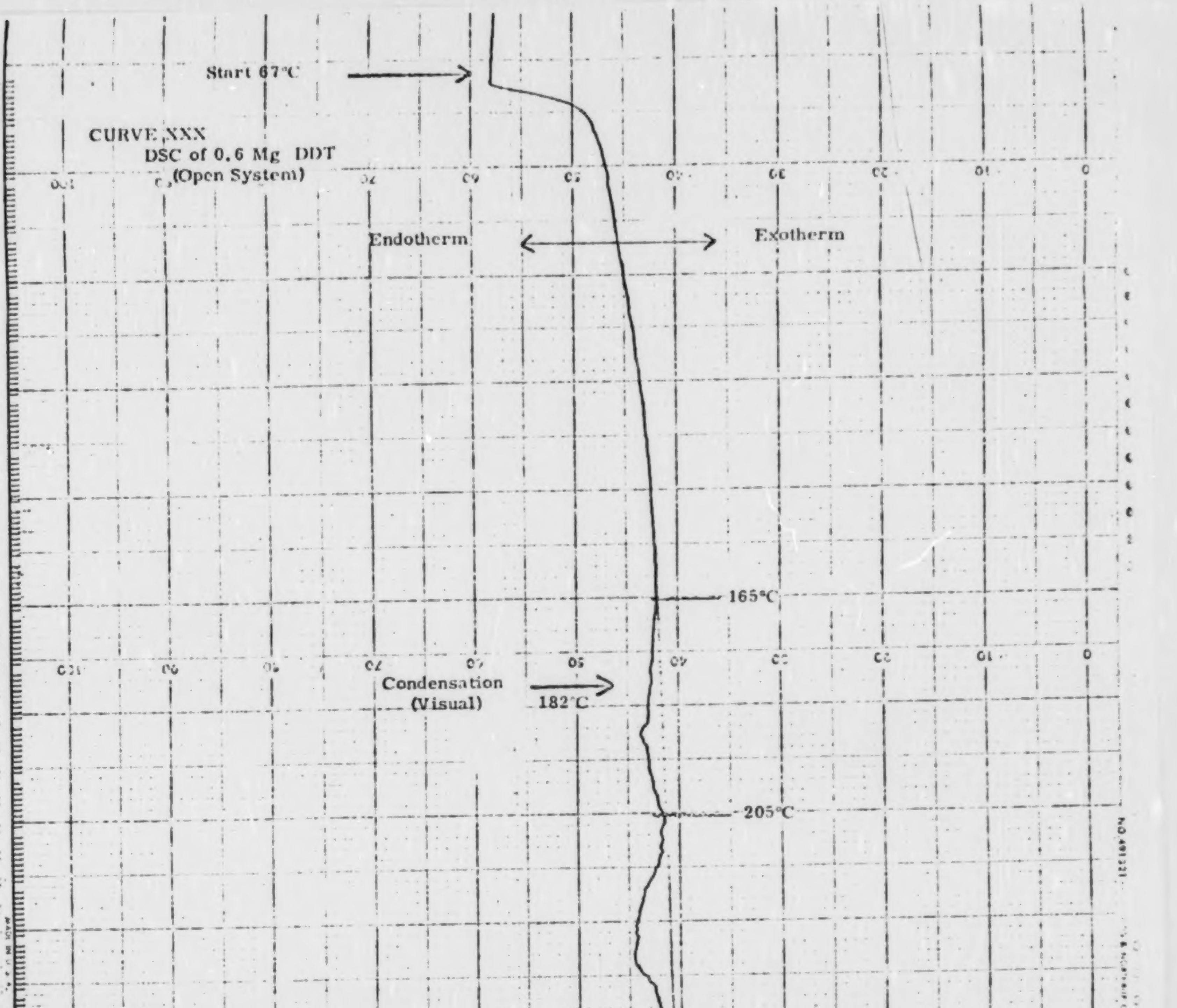


CURVE XXVII
DSC of 1.0 mg Pentachloronitrobenzene
(Closed System)


Start 87°C
CURVE XXVIII
DSC of 2.3 Mg KNO3
1.3 Mg PCNB
(Closed System)
Endotherm
Exotherm
136°C
Intercrystilline Change KNO3/
Melting Pt PCNB
152°C
Condensation
(Visual)
320°C
Boiling Pt PCNB 328°C
with decomposition
Melting Pt KNO3
357°C
BLA
No Charring
End 500 C

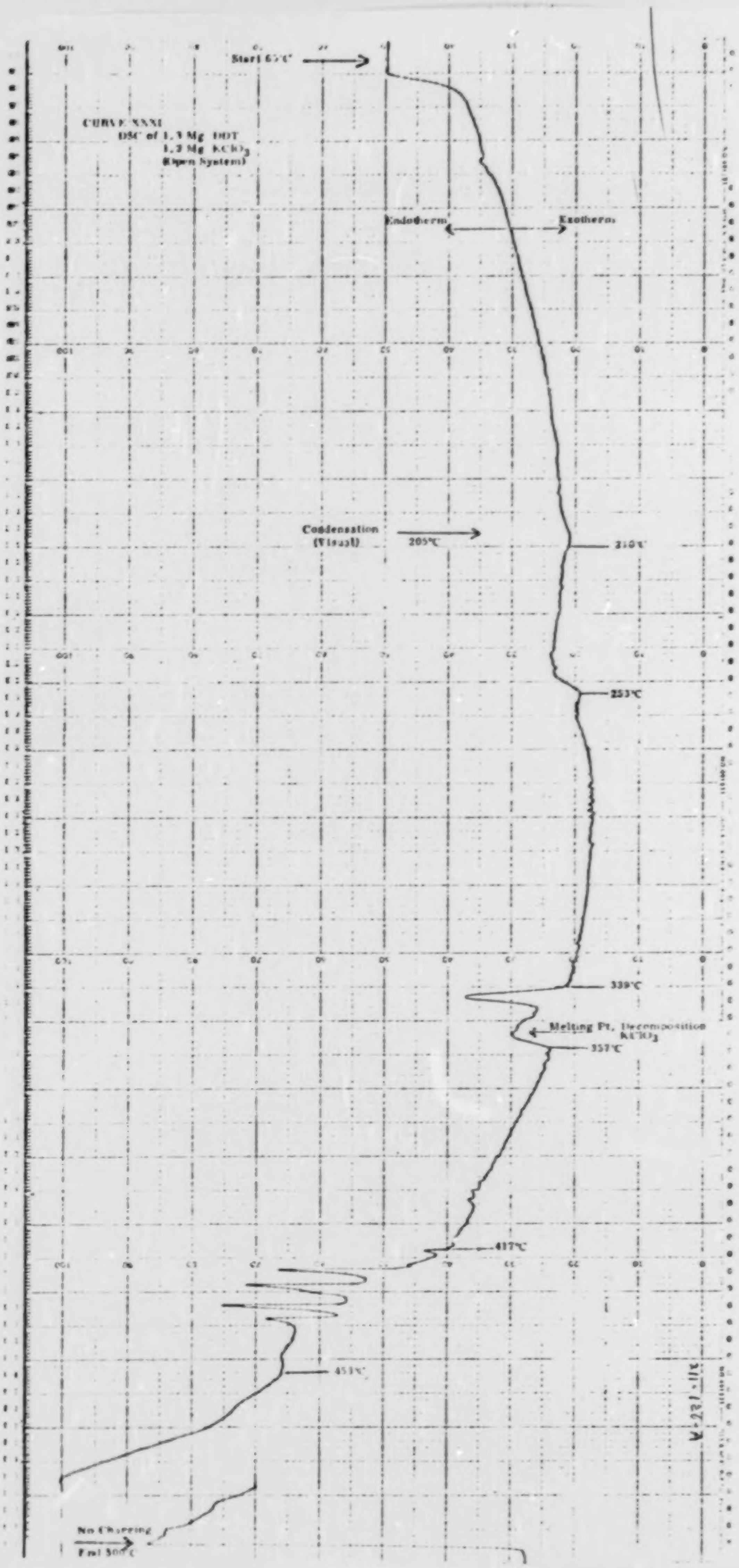


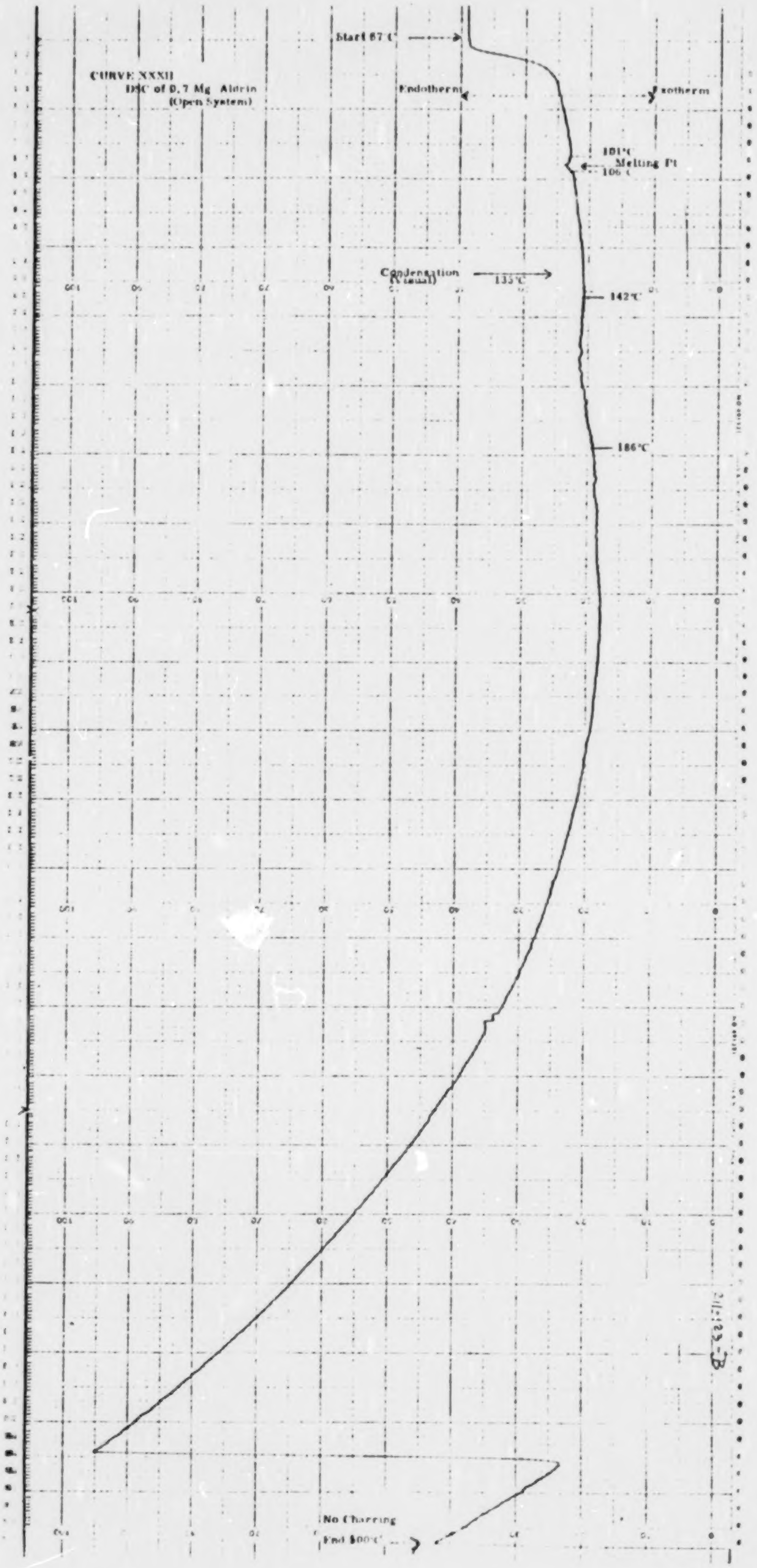
CURVE XXIX
DSC of 1.8 Mg $KClO_3$
1.2 Mg PCNB
(Closed System)



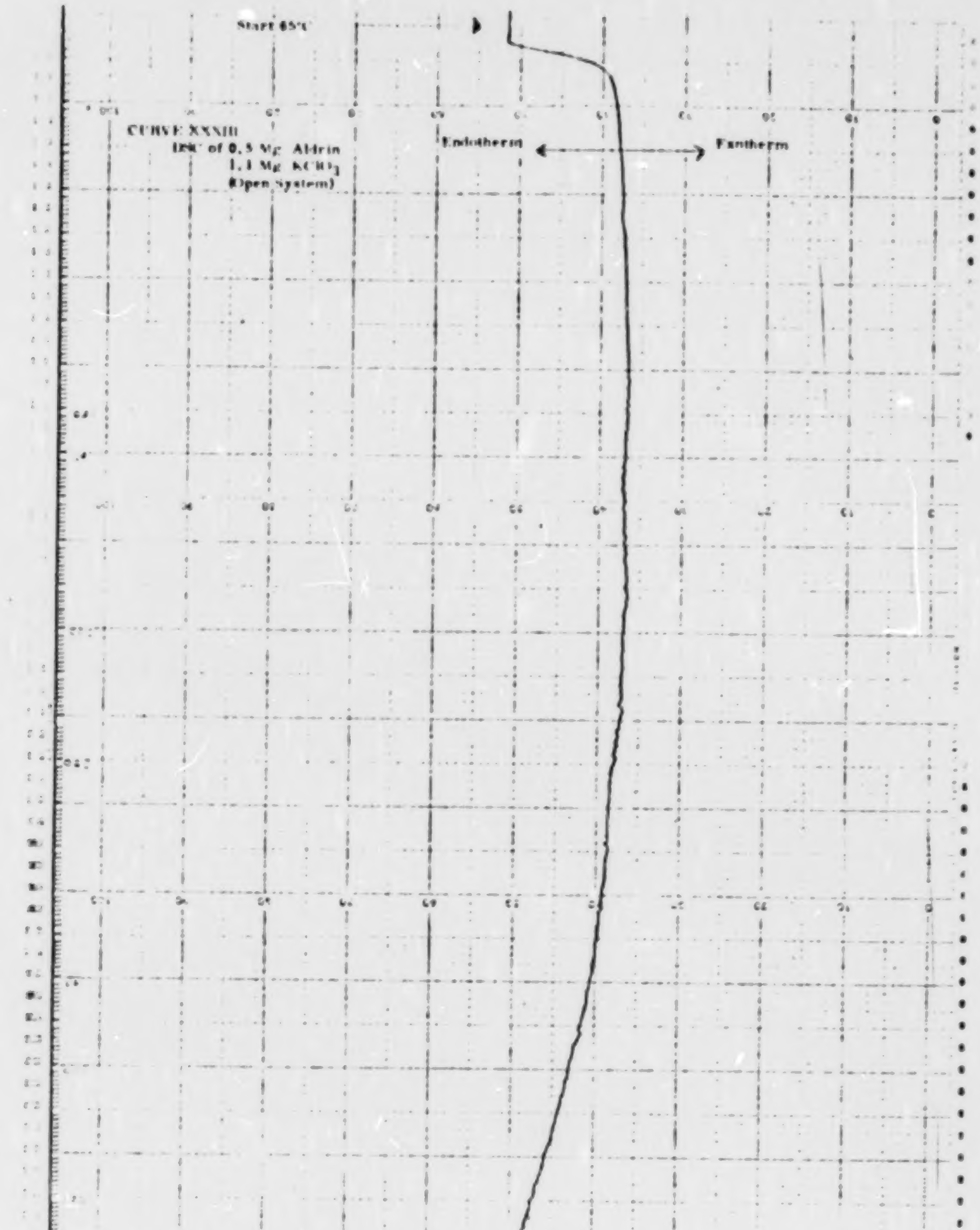
CURVE XXX
DSC of 0.6 Mg DDT
(Open System)

211-122-A

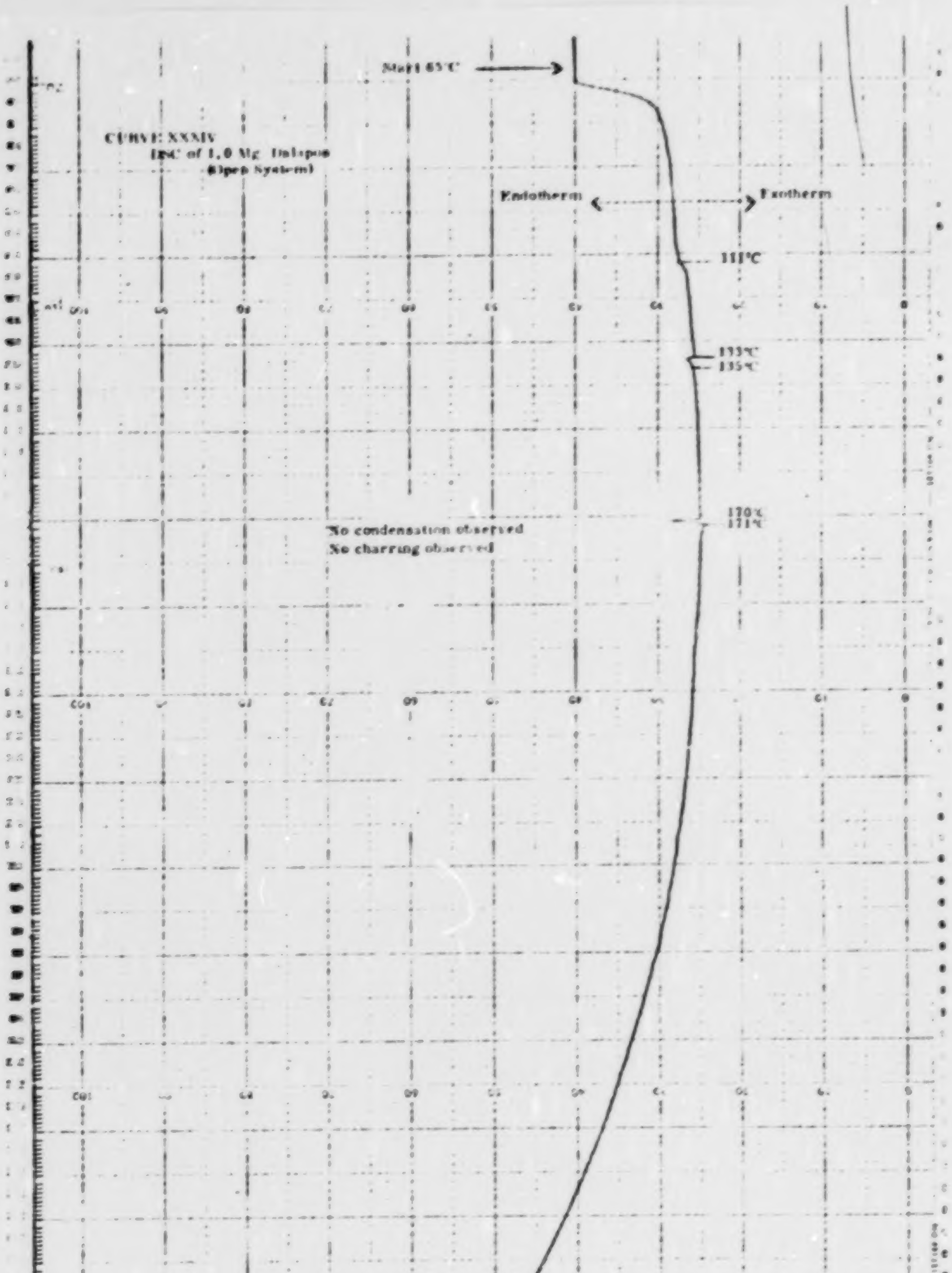

Start 65°C
CURVE XXXI
DSC of 1.3 Mg DDT
1.2 Mg $KClO_3$
(Open System)
Endotherm
Exotherm
Condensation
(Visual)
205°C
210°C
253°C
339°C
Melting Pt. Decomposition
$KClO_3$
357°C
417°C
453°C
No Charring
End 500°C

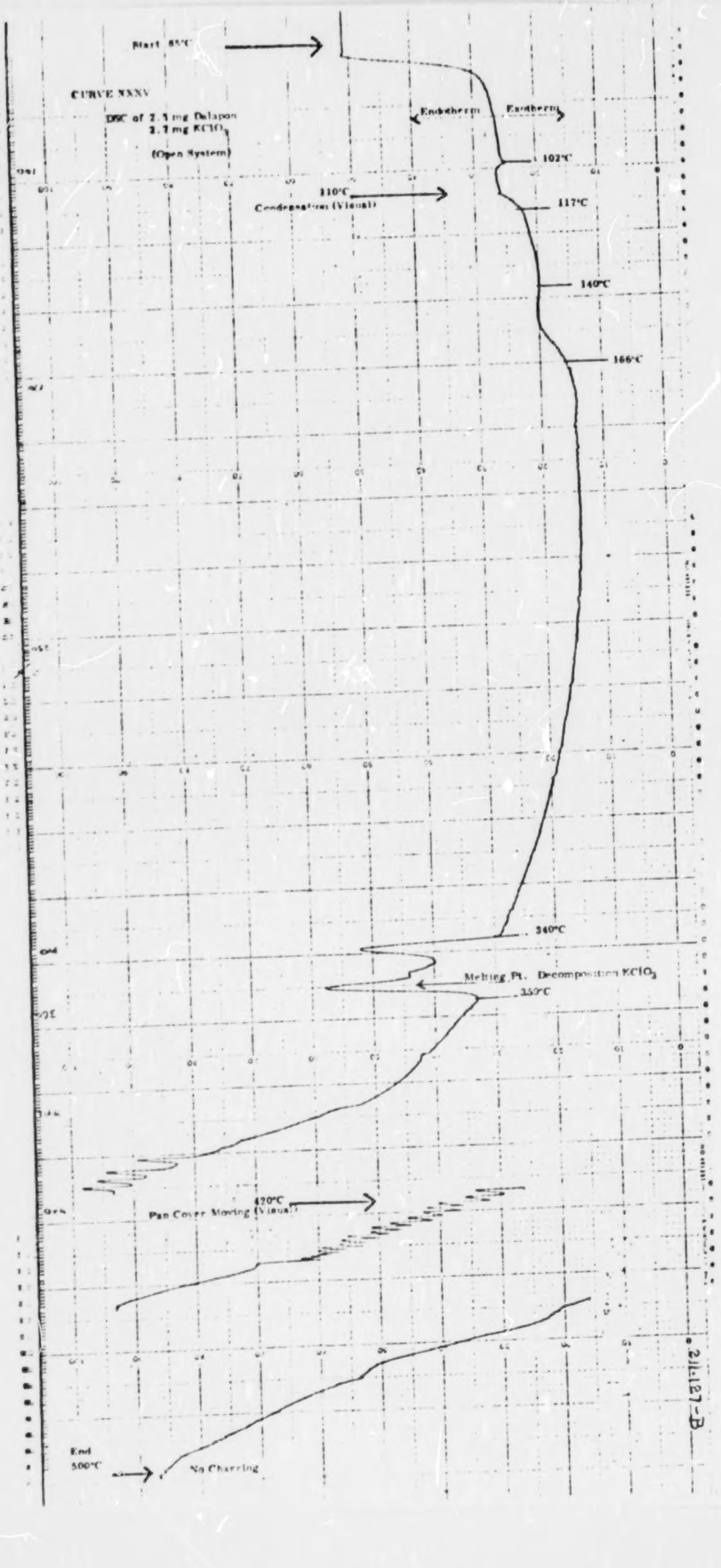


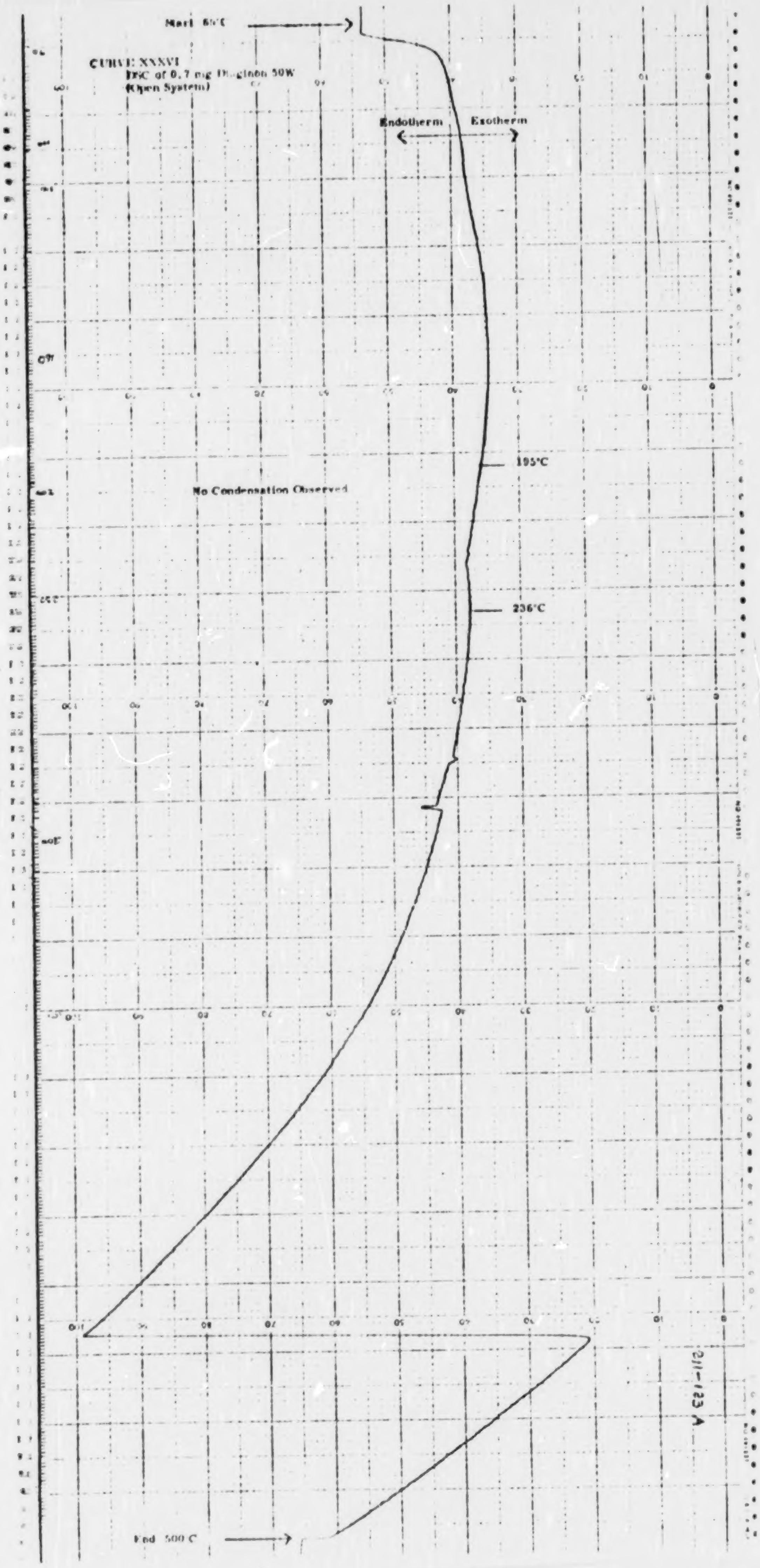
CURVE XXXII
DSC of 0.7 Mg Aldrin
(Open System)

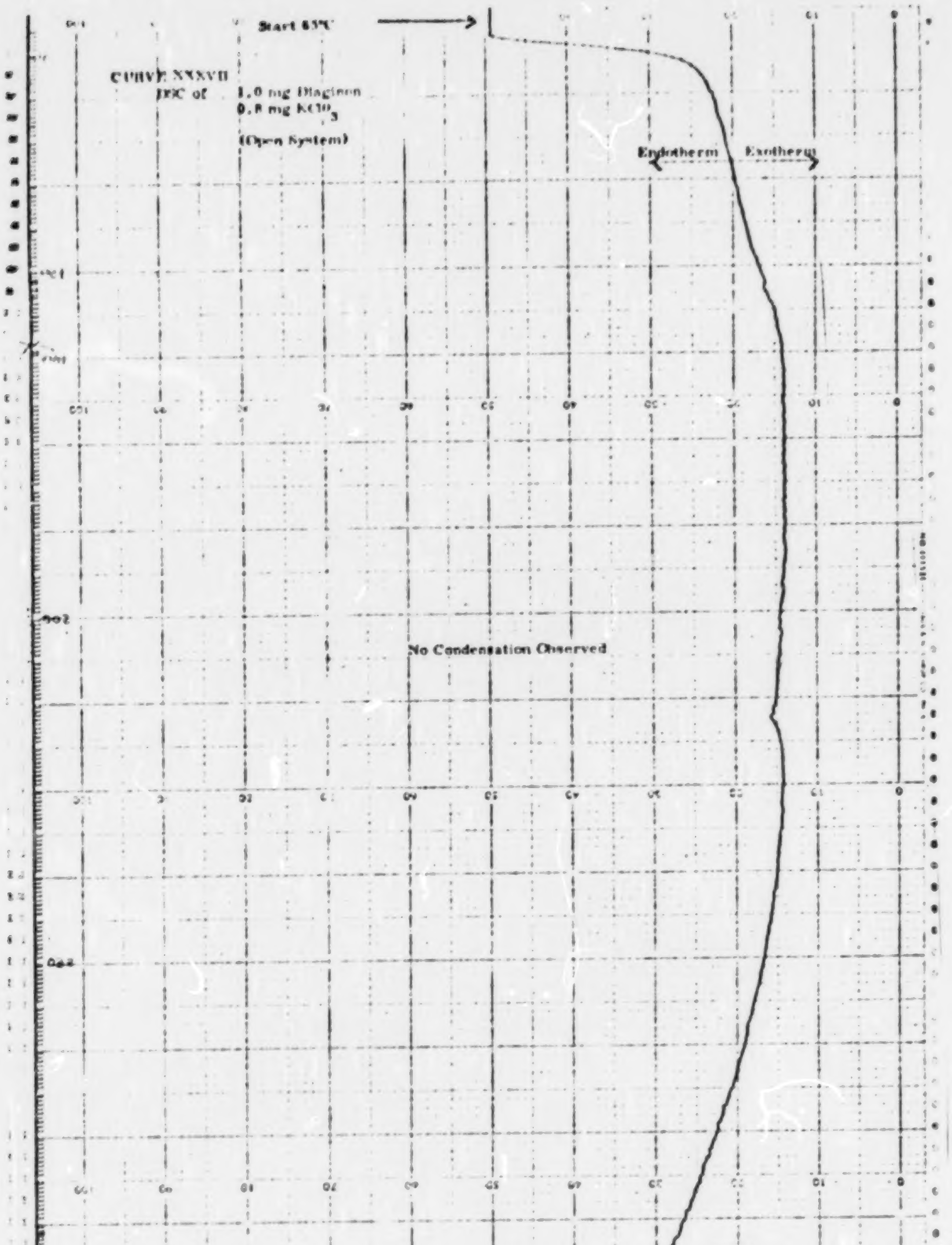


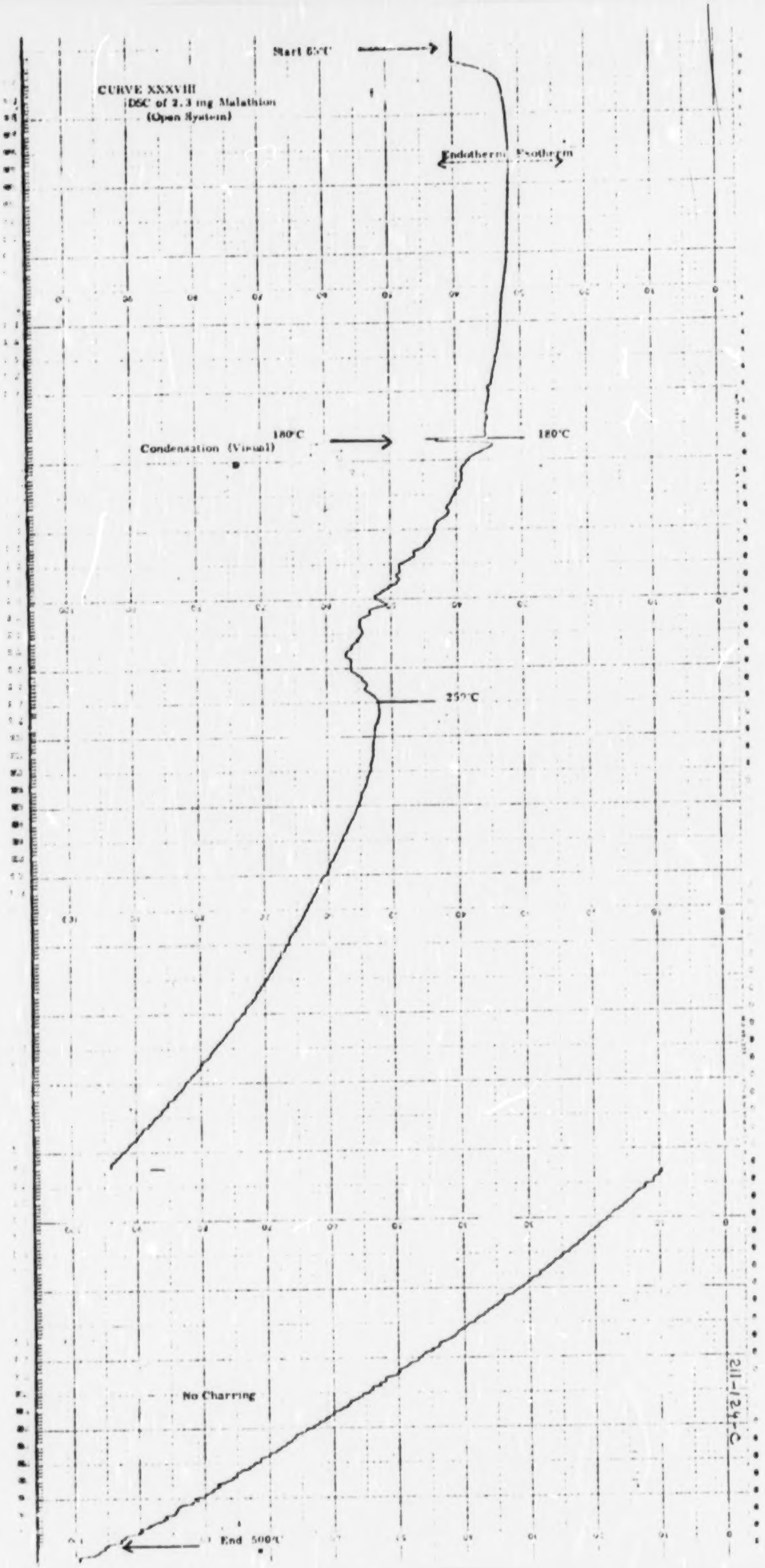
CURVE XXXIII
DTA of 0.5 Mg Aldrin
1.1 Mg $KClO_3$
(Open System)


CURVE XXXIV
DSC of 1.0 Mg Dalapon
(Open System)
Start 65°C
Endotherm
Exotherm
111°C
133°C
135°C
170°C
171°C
No condensation observed
No charring observed
End 500°C

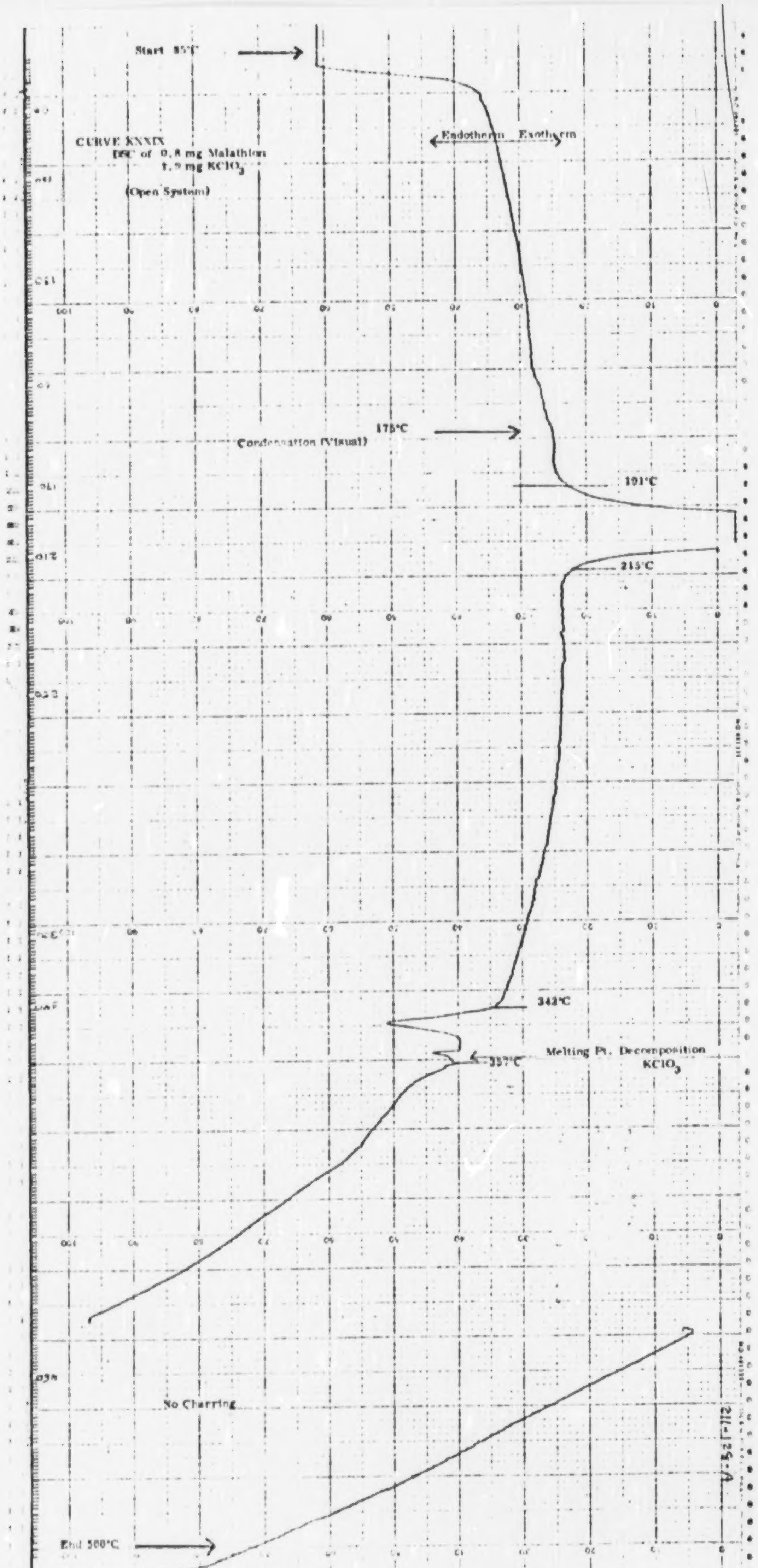

CURVE XXXV
DSC of 2.1 mg Dalapon
2.7 mg $KClO_3$
(Open System)
Start 85°C
Endotherm
Exotherm
102°C
110°C
Condensation (Visual)
117°C
140°C
166°C
340°C
Melting Pt. Decomposition $KClO_3$
350°C
420°C
Pan Cover Moving (Visual)
End
500°C
No Charring
211:127-B


Start 60°C
CURVE XXXVI
DSC of 0.7 mg Diazinon 50W
(Open System)
Endotherm
Exotherm
195°C
No Condensation Observed
236°C
End 500°C
211-123 A

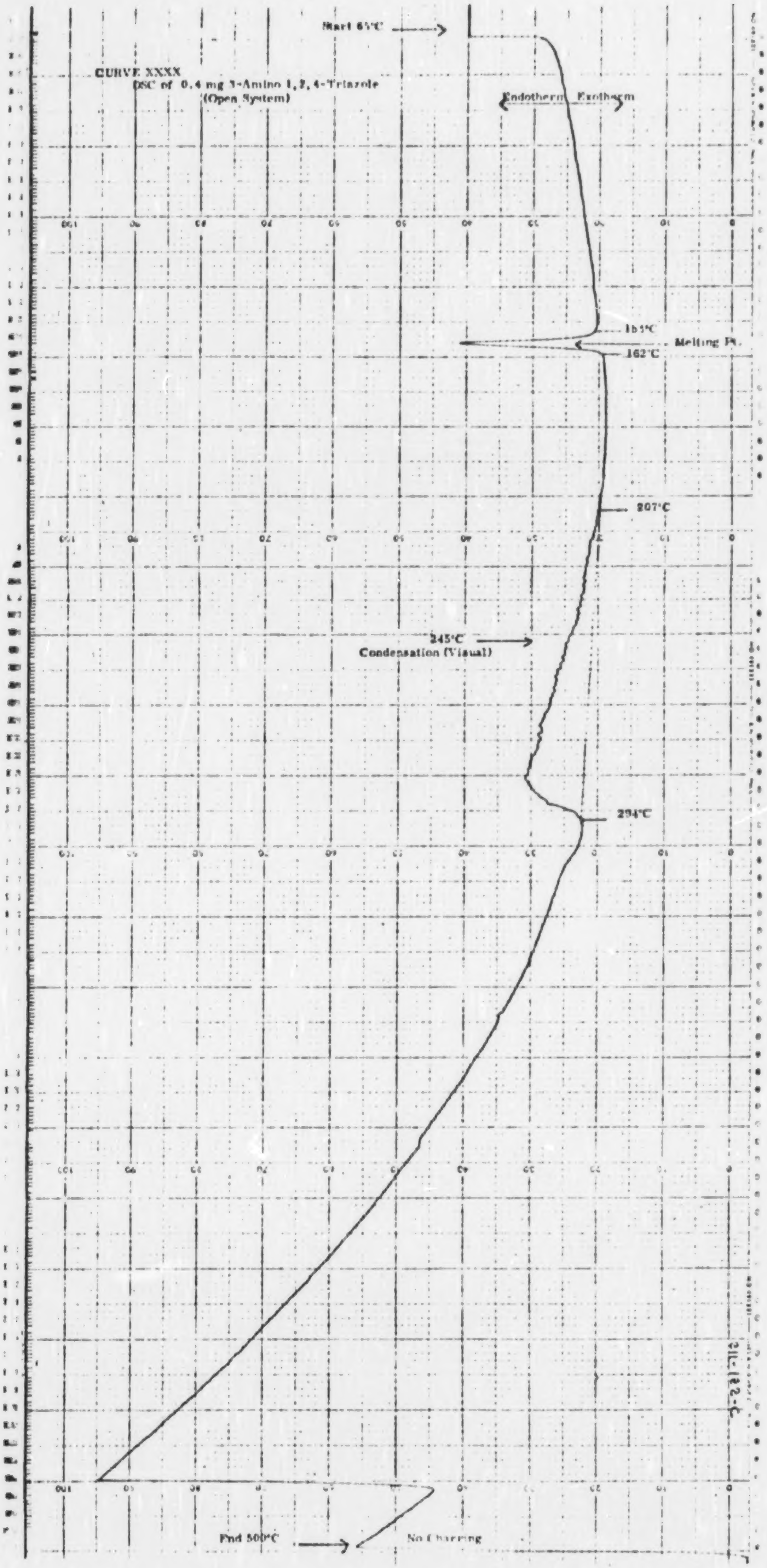

CURVE XXXVII
DTC of 1.0 mg Diazinon
0.8 mg $KClO_3$
(Open System)
Start 65°C
Endotherm
Exotherm
No Condensation Observed
351°C
Melting Pt. Decomposition $KClO_3$
361°C
371°C
397°C
End 500°C
No Charring

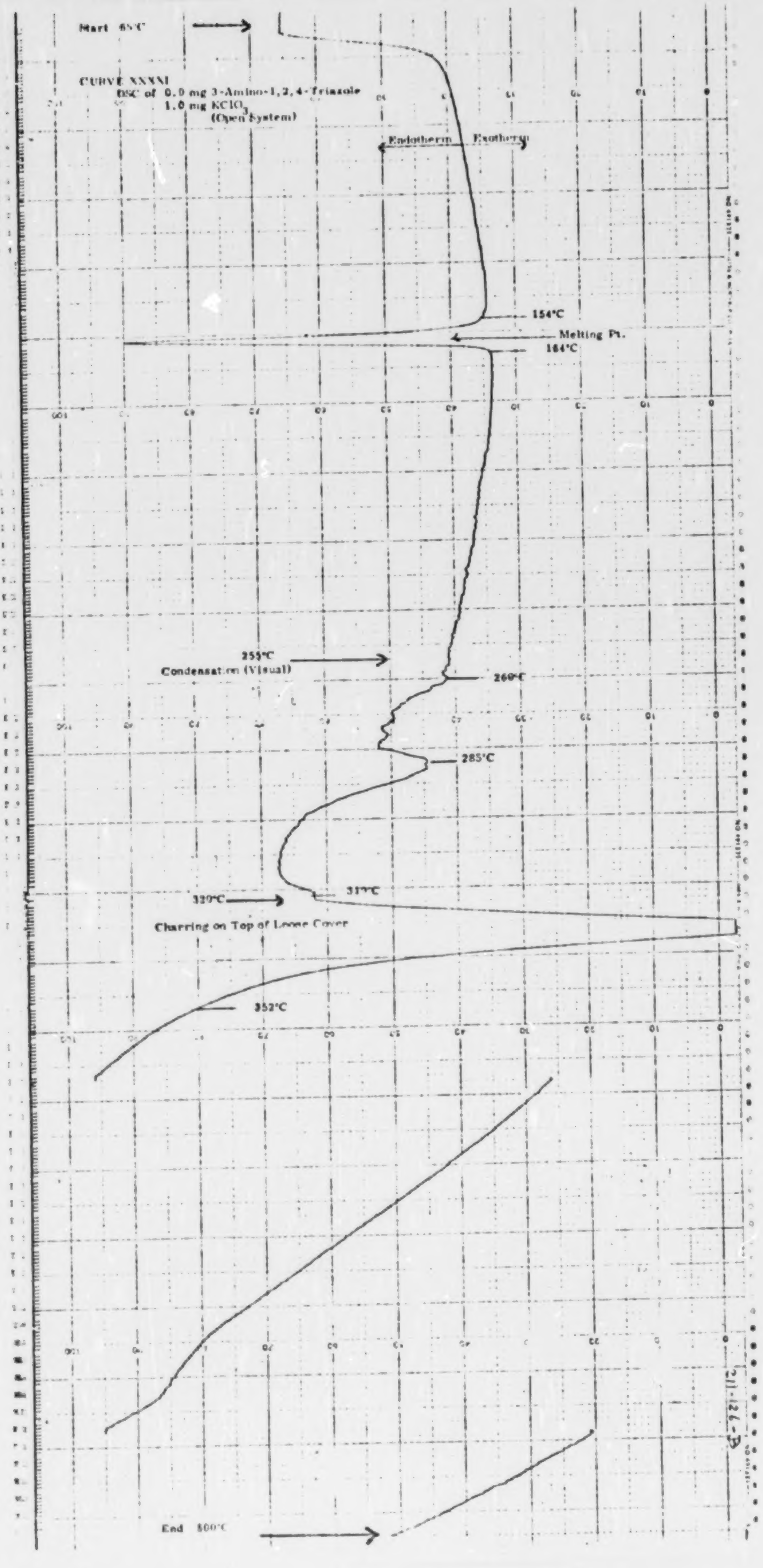


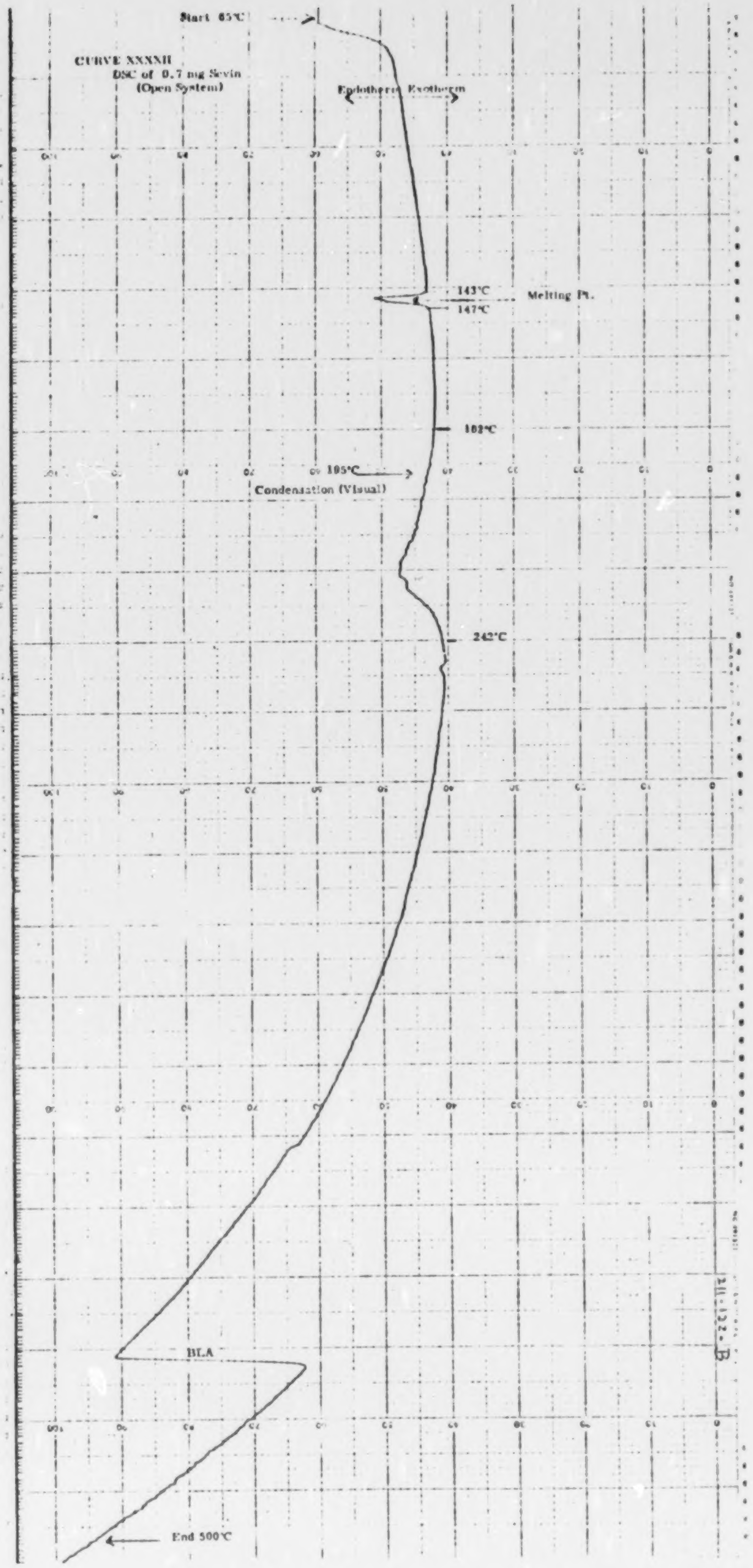
CURVE XXXVIII
DSC of 2.3 mg Malathion
(Open System)

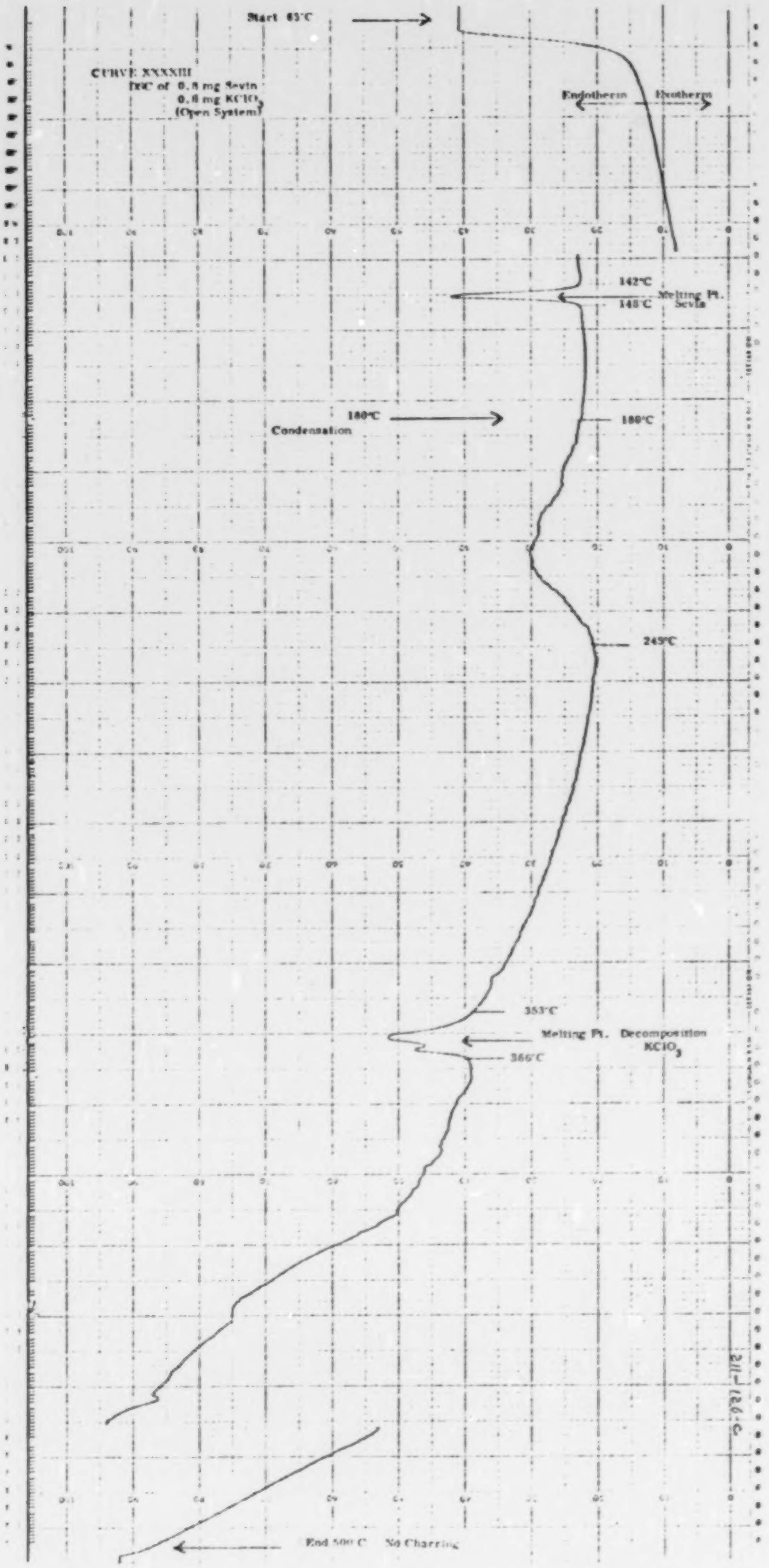


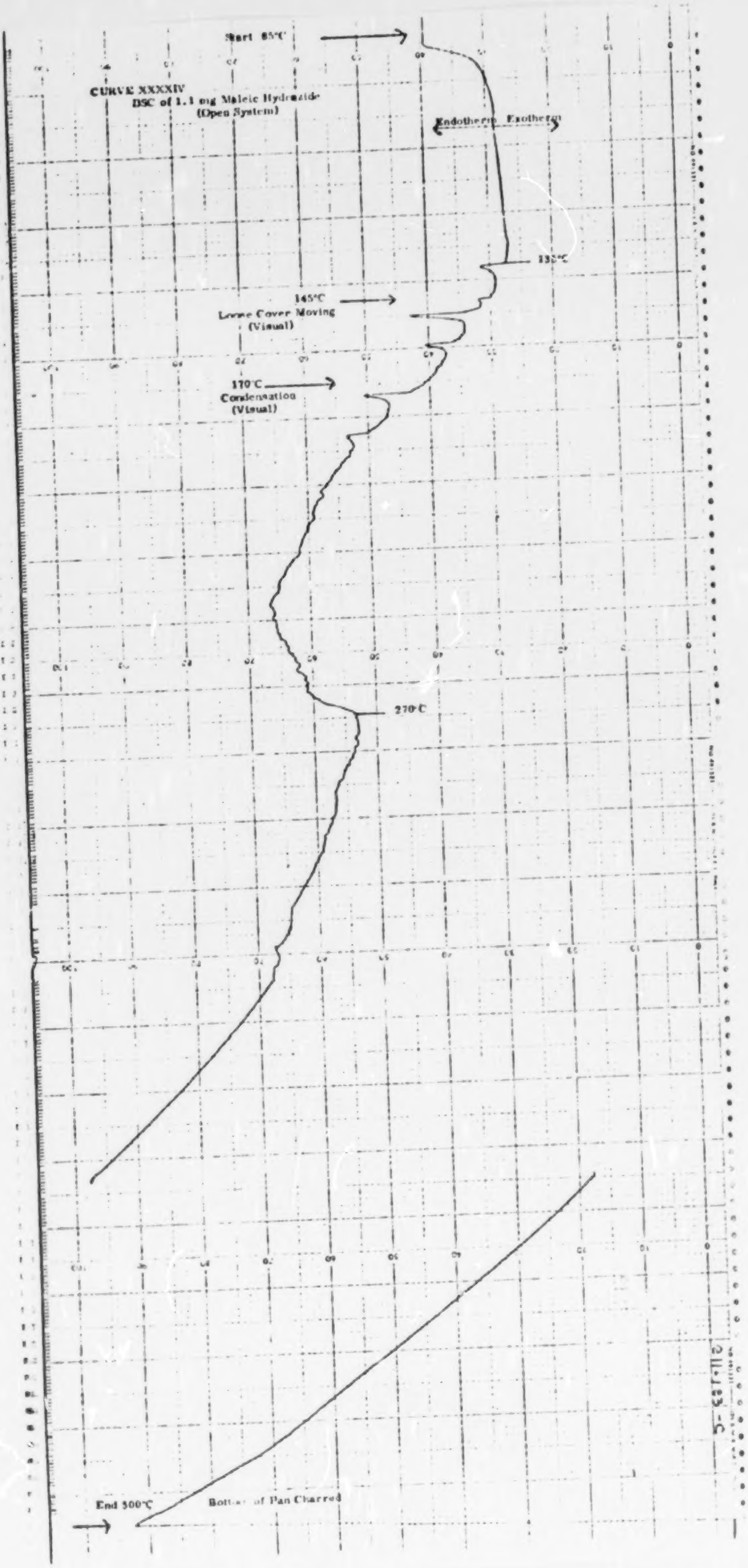
CURVE XXXIX
DSC of 0.8 mg Malathion
1.9 mg $KClO_3$
(Open System)

CURVE XXXX
DSC of 0.4 mg 3-Amino 1,2,4-Triazole
(Open System)
Start 65°C
Endotherm Exotherm
159°C
Melting Pt.
162°C
207°C
245°C
Condensation (Visual)
294°C
End 500°C
No Charring
100
90
80
70
60
50
40
30
20
10
0

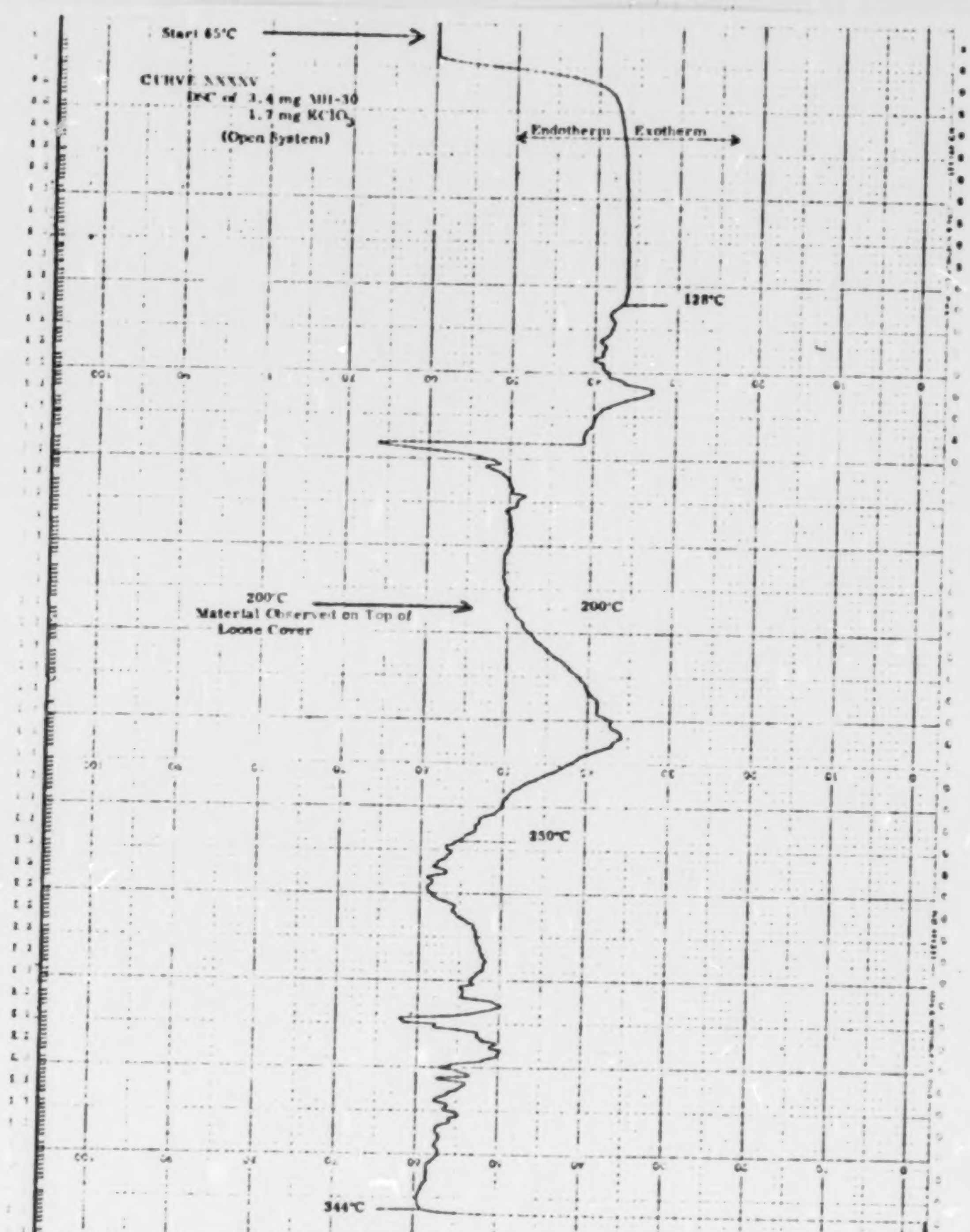

Start 65°C
CURVE XXXXI
DSC of 0.9 mg 3-Amino-1,2,4-Triazole
1.0 mg $KClO_3$
(Open System)
Endotherm
Exotherm
154°C
Melting Pt.
164°C
255°C
Condensation (Visual)
260°C
285°C
317°C
320°C
Charring on Top of Loose Cover
352°C
End 500°C

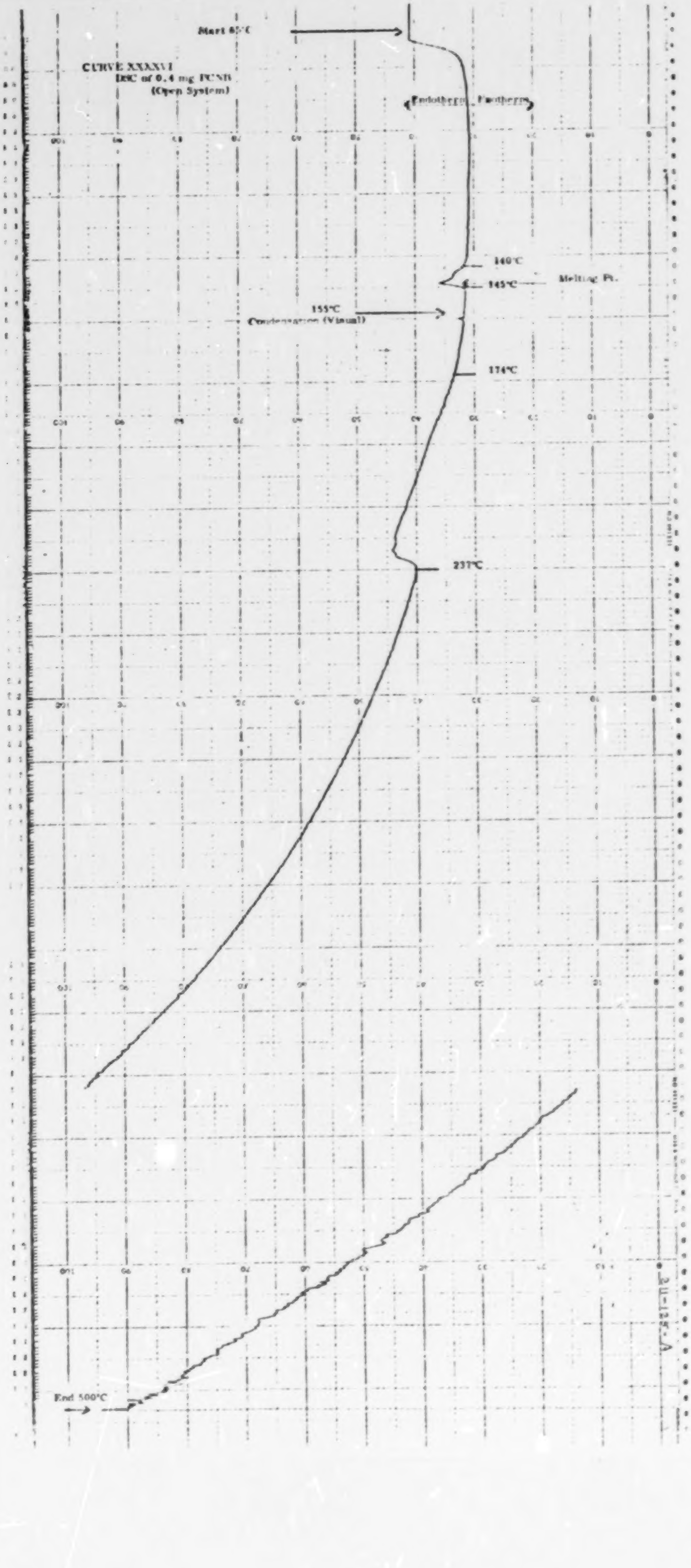

Start 65°C
CURVE XXXXII
DSC of 0.7 mg Sevin
(Open System)
Endotherm Exotherm
143°C
Melting Pt.
147°C
182°C
195°C
Condensation (Visual)
242°C
BLA
End 500°C


Start 65°C
CURVE XXXXIII
DTA of 0.8 mg Sevin
0.8 mg $KClO_3$
(Open System)
Endotherm
Exotherm
142°C
148°C
Melting Pt. Sevin
180°C
Condensation
180°C
245°C
353°C
Melting Pt. Decomposition $KClO_3$
366°C
End 500°C No Charring
C-9321-112

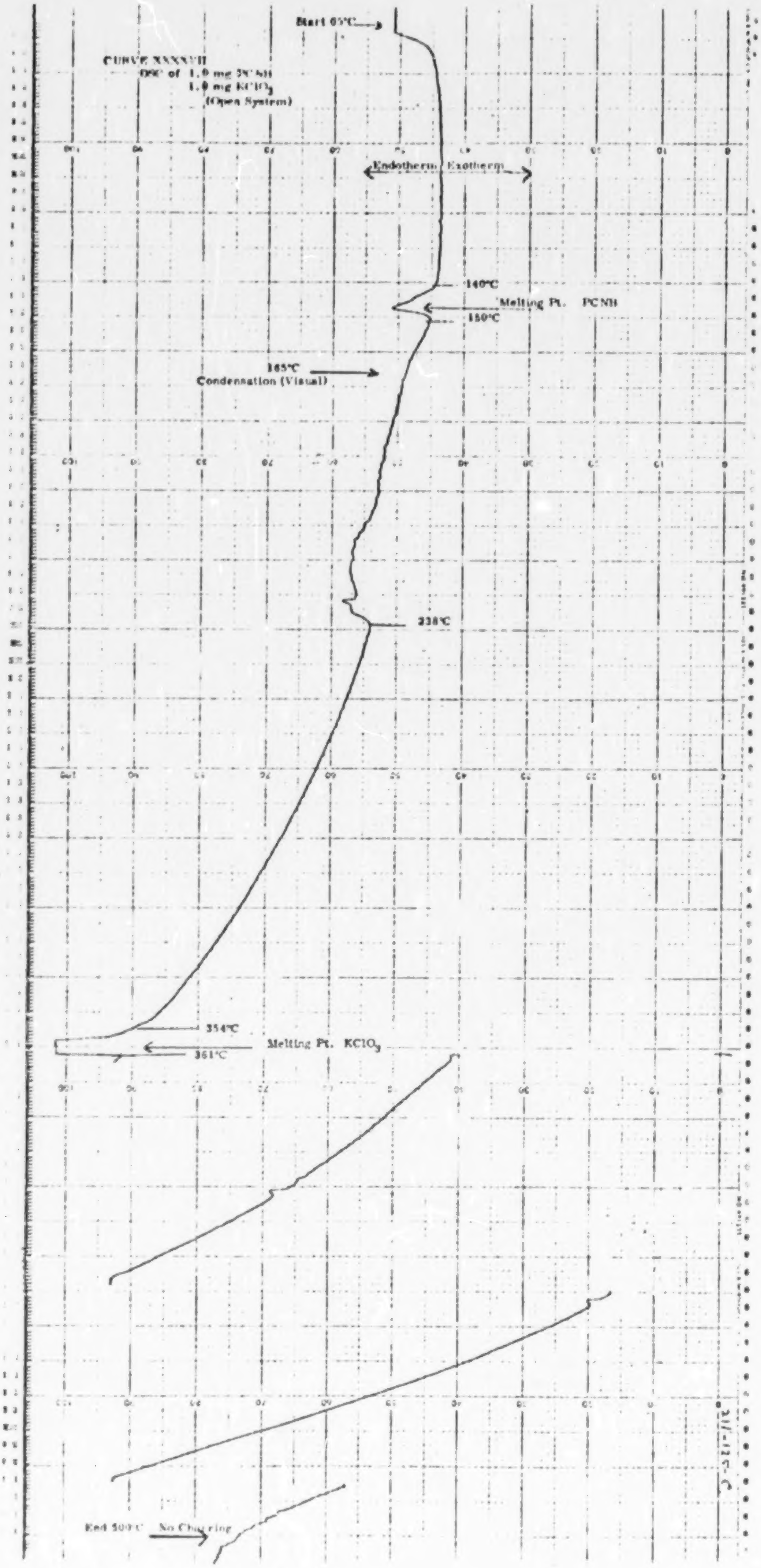


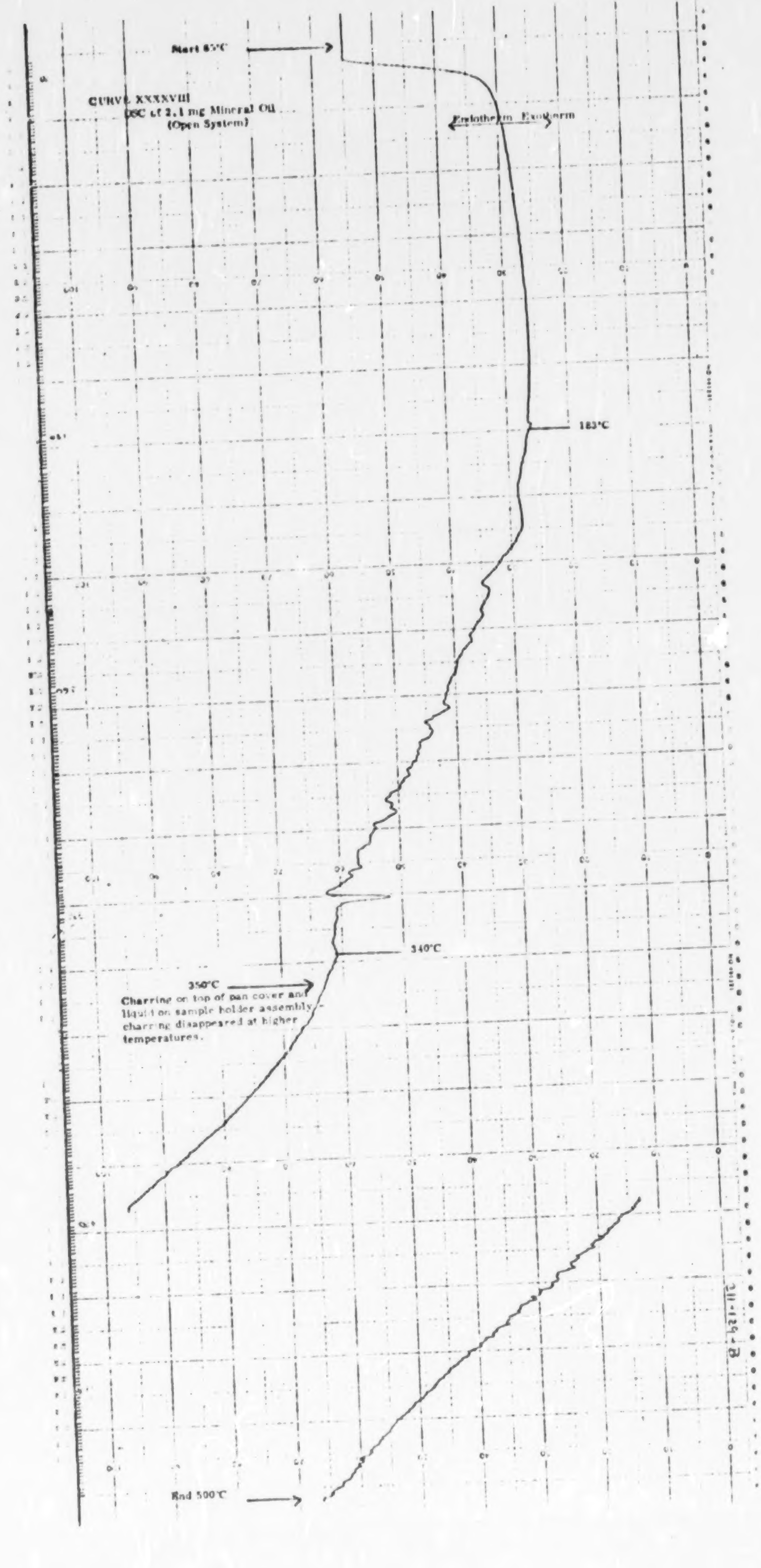
CURVE XXXXIV
DSC of 1.1 mg Maleic Hydrazide
(Open System)


Start 65°C
CURVE XXXXV
DSC of 3.4 mg MH-30
1.7 mg $KClO_3$
(Open System)
Endotherm
Exotherm
128°C
200°C
Material Observed on Top of
Loose Cover
200°C
250°C
344°C
357°C
378°C
End 500°C
Charring

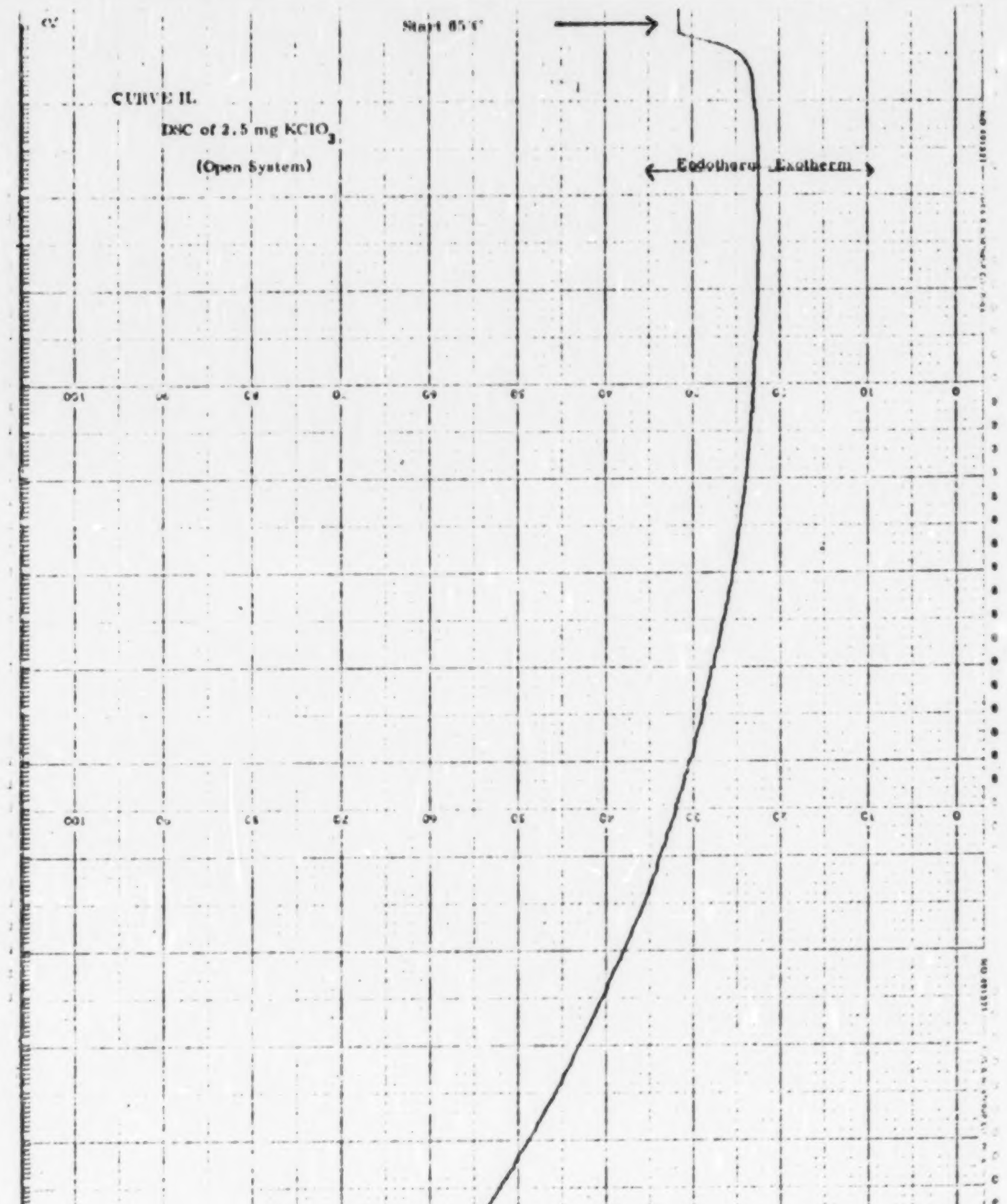


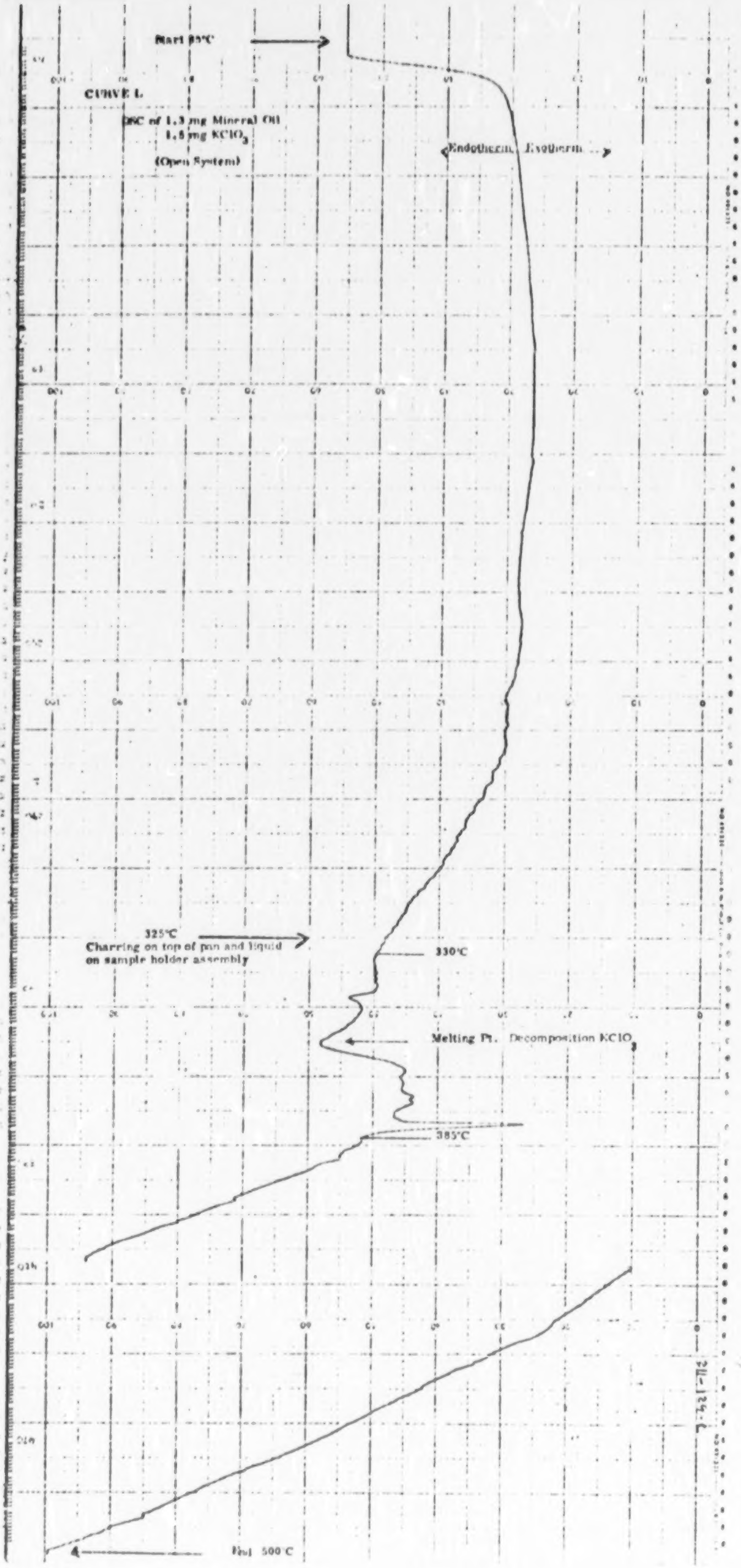
CURVE XXXXVI
DSC of 0.4 mg PCNB
(Open System)

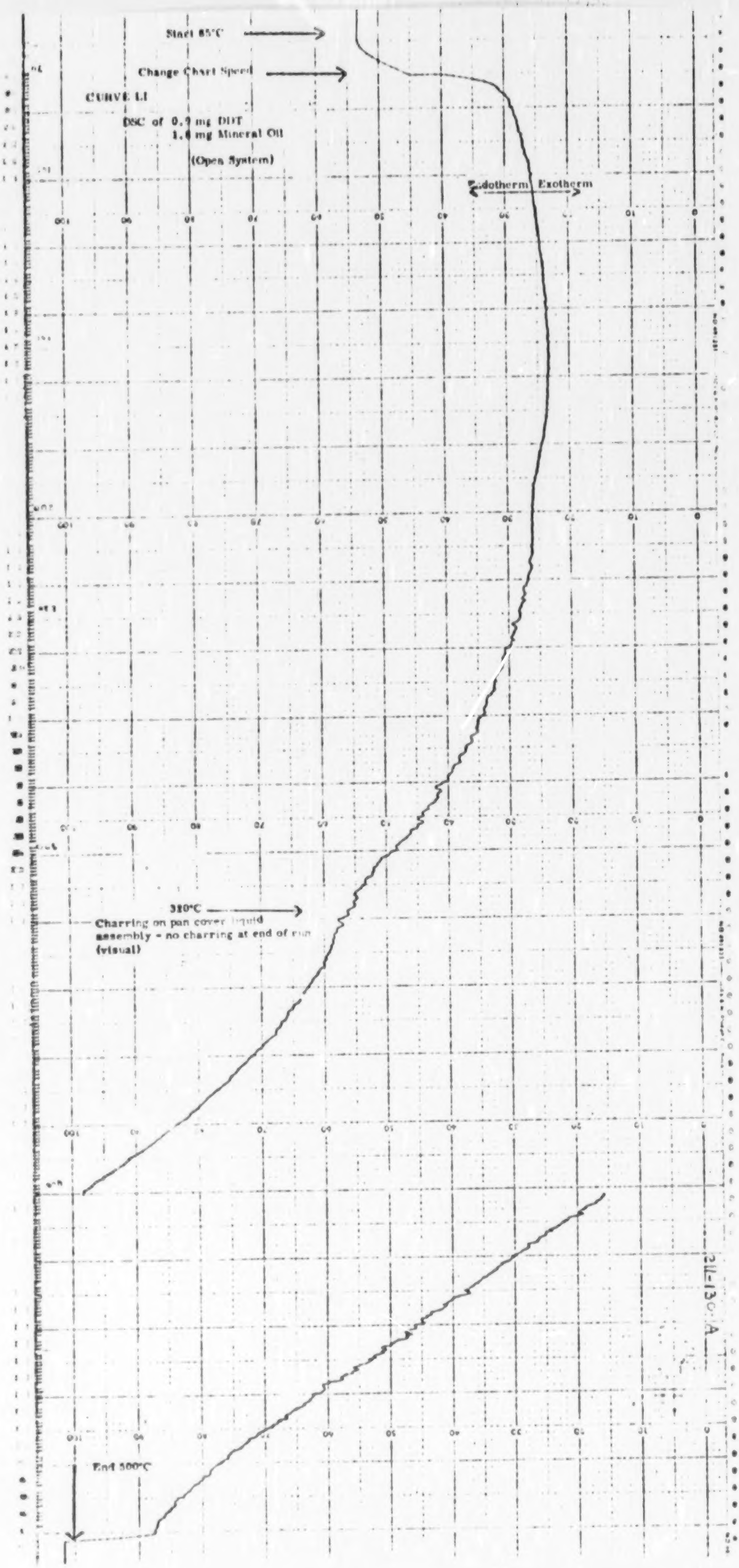

CURVE XXXXVII
DSC of 1.0 mg PCNH
1.0 mg KClO3
(Open System)
Start 65°C
Endotherm
Exotherm
140°C
Melting Pt. PCNH
150°C
165°C
Condensation (Visual)
238°C
354°C
Melting Pt. KClO3
361°C
End 500°C
No Charring

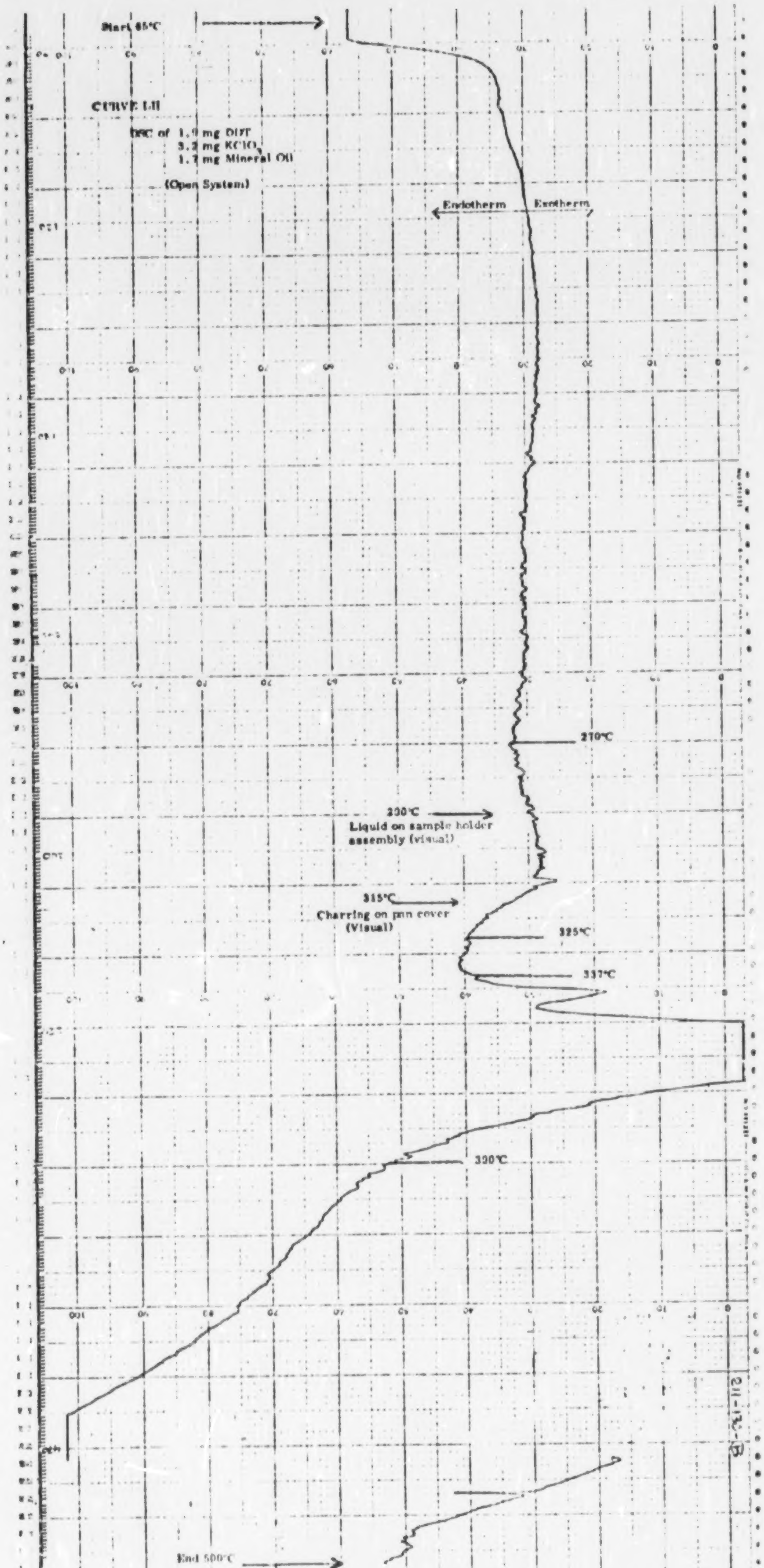


CURVE XXXXVIII
DSC of 2.1 mg Mineral Oil
(Open System)


CURVE II.
DSC of 2.5 mg KClO3
(Open System)
Start 85°C
Endotherm Exotherm
100 90 80 70 60 50 40 30 20 10 0
355°C
Melting Pt. Decomposition KClO3
363°C
End 445°C
211-125-B


Start 35°C
CURVE L
DSC of 1.3 mg Mineral Oil
1.5 mg $KClO_3$
(Open System)
Endotherm Exotherm
325°C
Charring on top of pan and liquid
on sample holder assembly
330°C
Melting Pt. Decomposition $KClO_3$
385°C
End 500°C

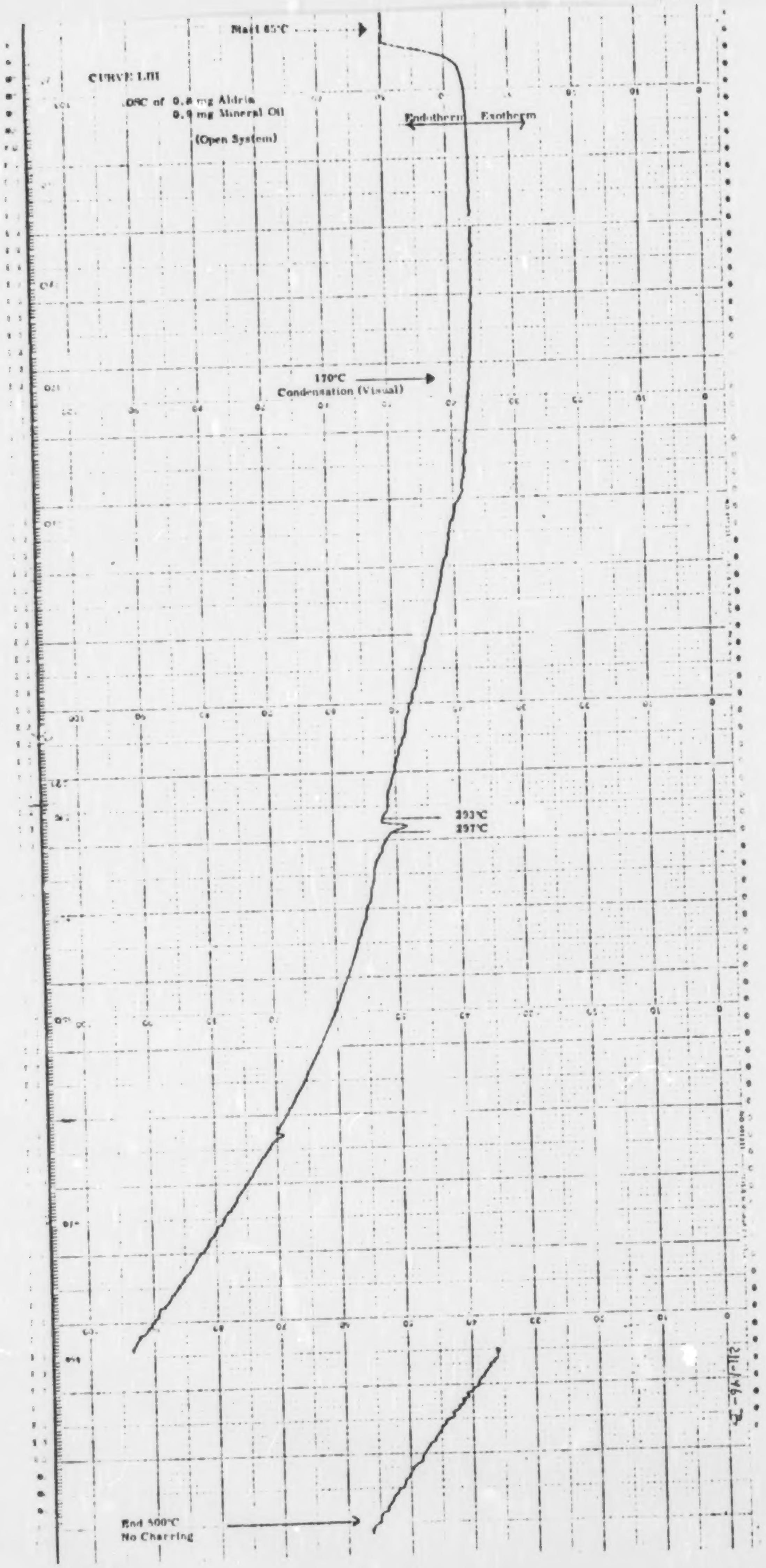

Start 85°C
Change Chart Speed
CURVE LI
DSC of 0.9 mg DDT
1.6 mg Mineral Oil
(Open System)
Endotherm Exotherm
320°C
Charring on pan cover liquid
assembly - no charring at end of run
(visual)
End 500°C
21L-130-A

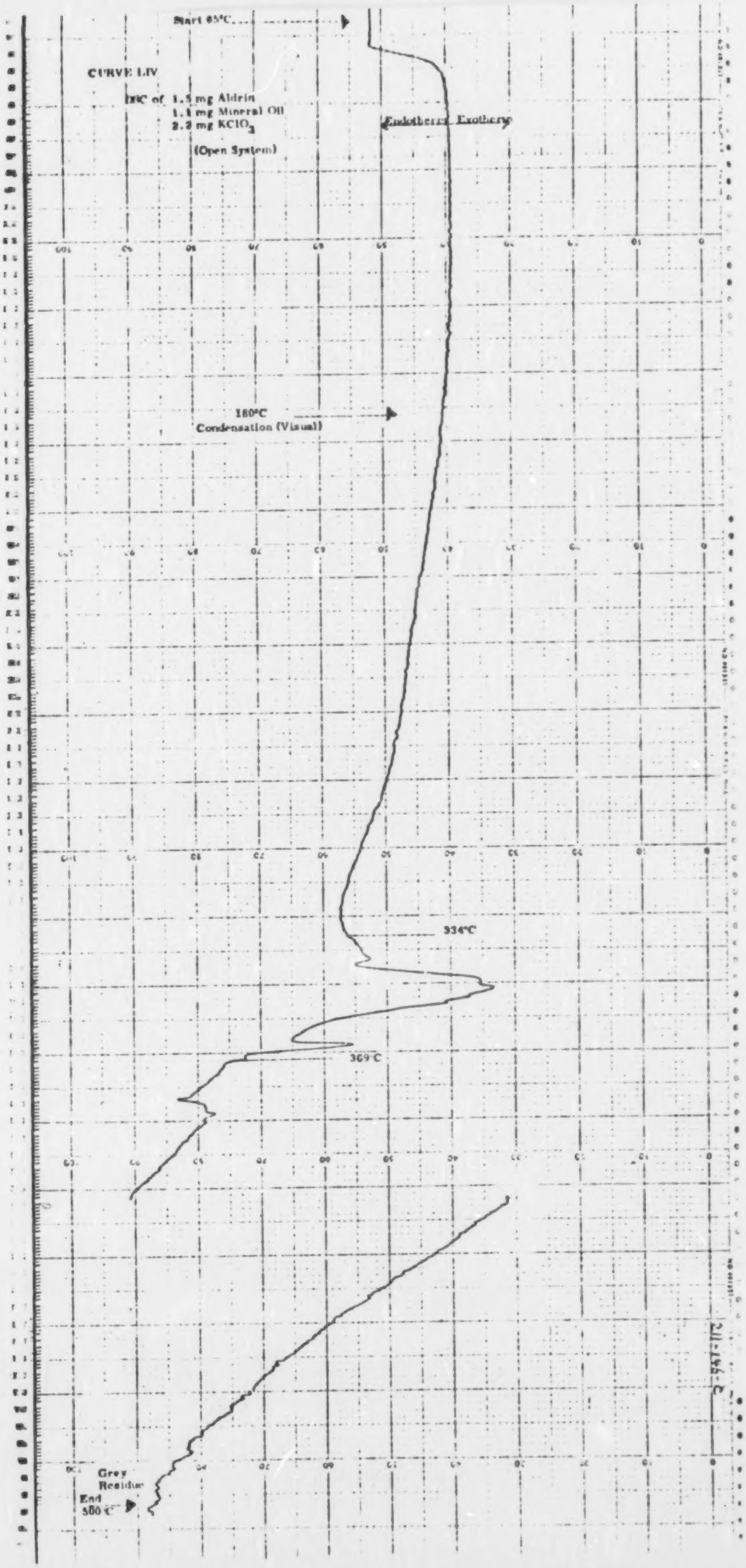


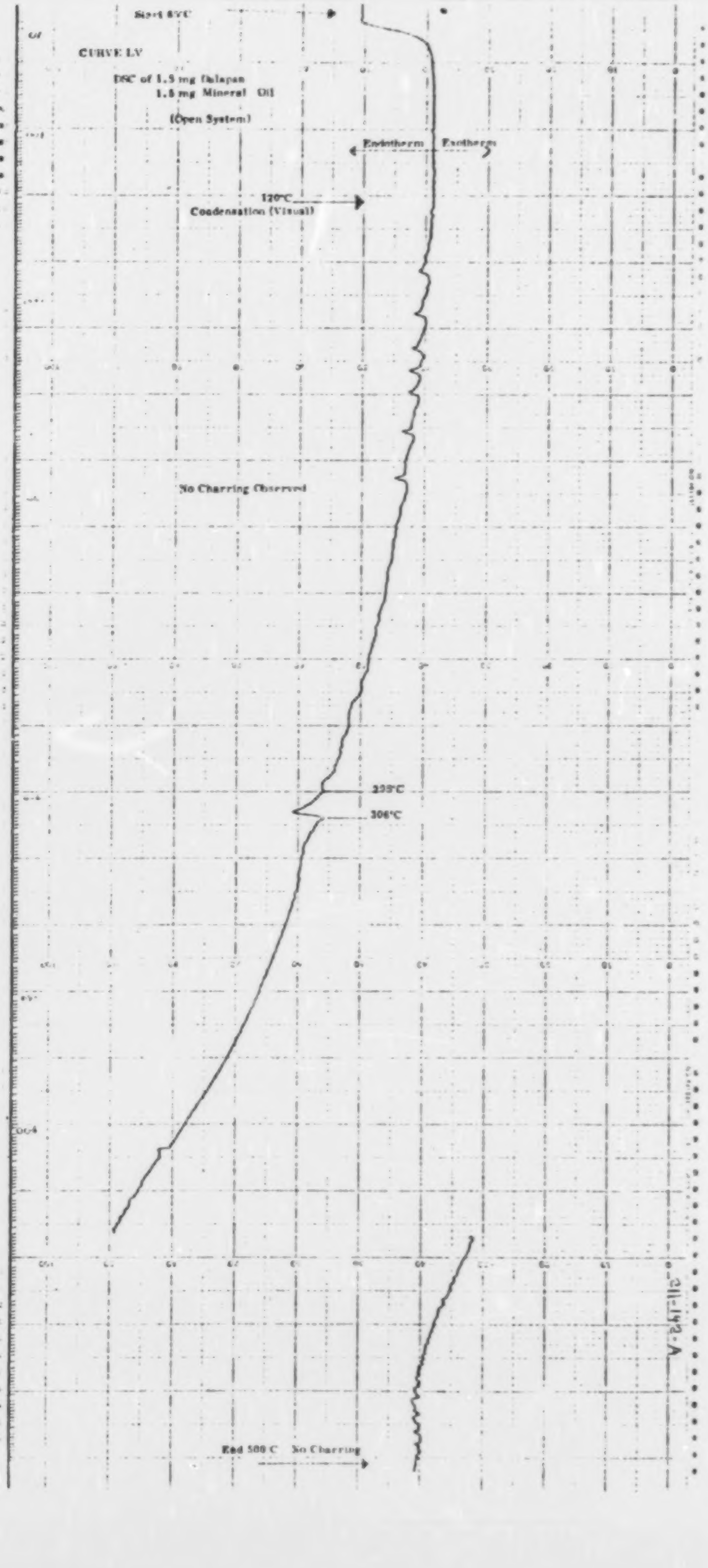
CURVE LII

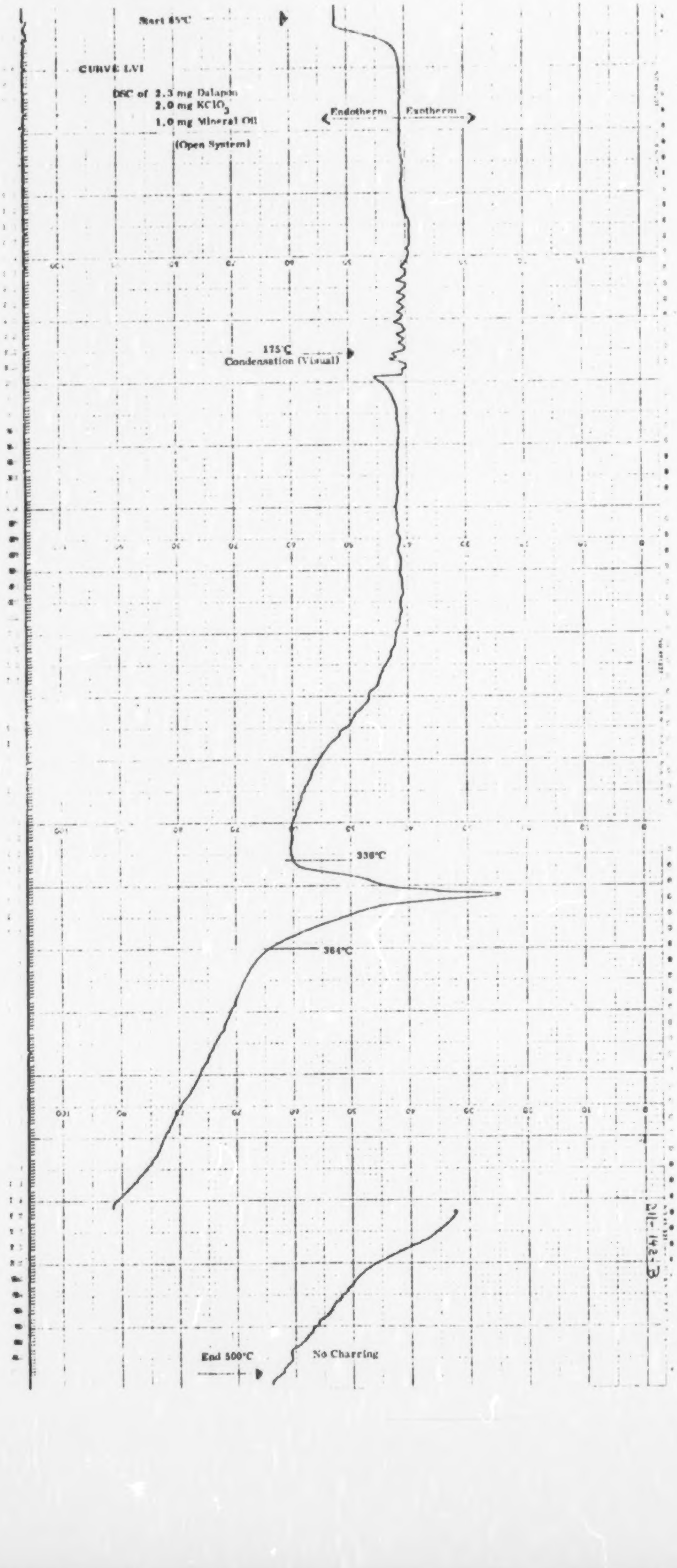
DSC of 1.9 mg DDT
3.2 mg $KClO_3$
1.7 mg Mineral Oil

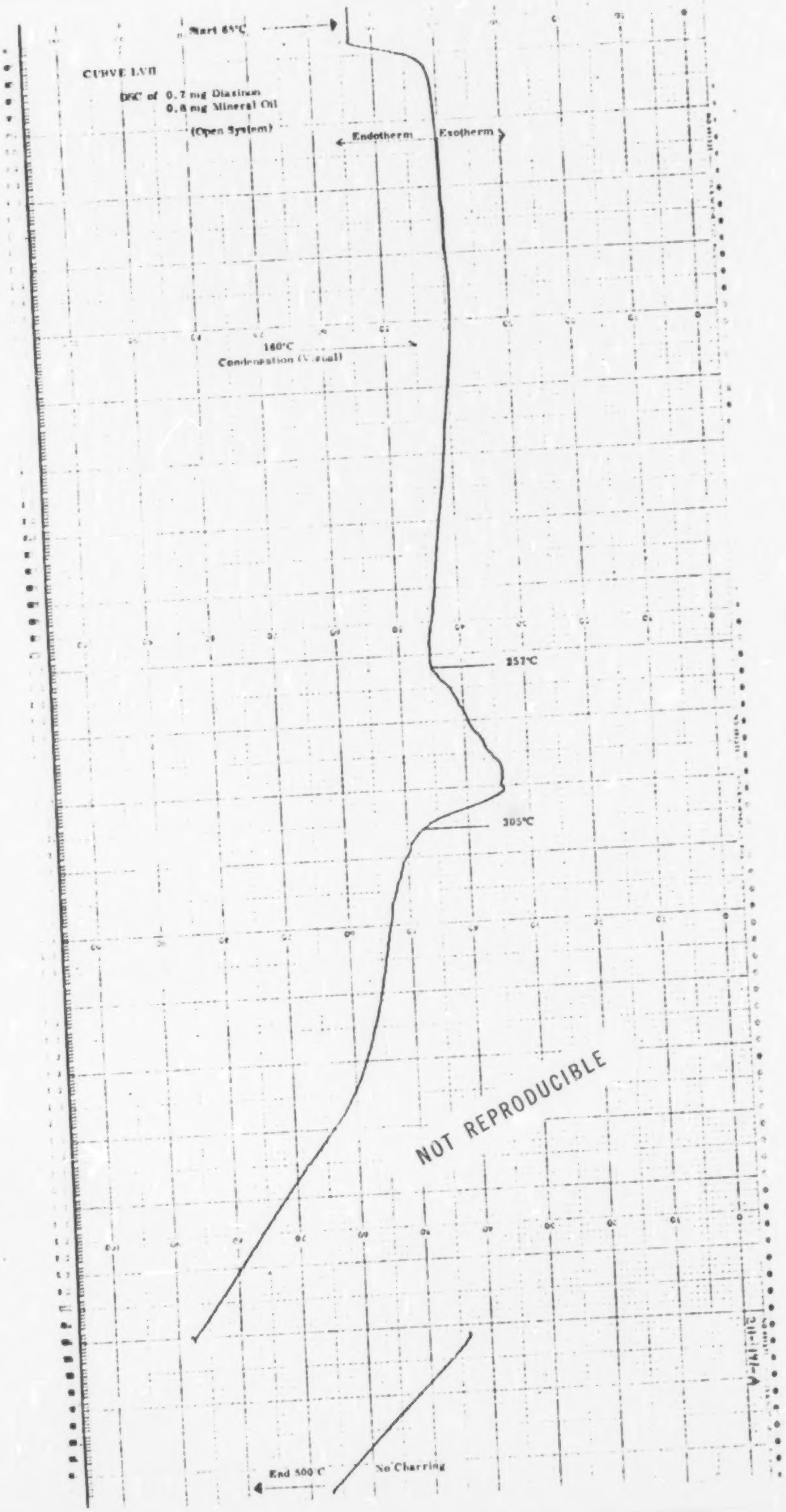
(Open System)


CURVE LIII
DSC of 0.8 mg Aldrin
0.9 mg Mineral Oil
(Open System)
Melt 65°C
Endotherm
Exotherm
170°C
Condensation (Visual)
293°C
297°C
End 500°C
No Charring


Start 85°C
CURVE LIV
DTA of 1.5 mg Aldrin
1.1 mg Mineral Oil
2.2 mg KClO$_3$
(Open System)
Endotherm Exotherm
180°C
Condensation (Visual)
334°C
369°C
Grey
Residue
End
500°C
211-196-C

Start 85°C
CURVE LV
DSC of 1.5 mg Dalapon
1.5 mg Mineral Oil
(Open System)
Endotherm
Exotherm
120°C
Condensation (Visual)
No Charring Observed
295°C
306°C
End 500°C No Charring
V-142-113

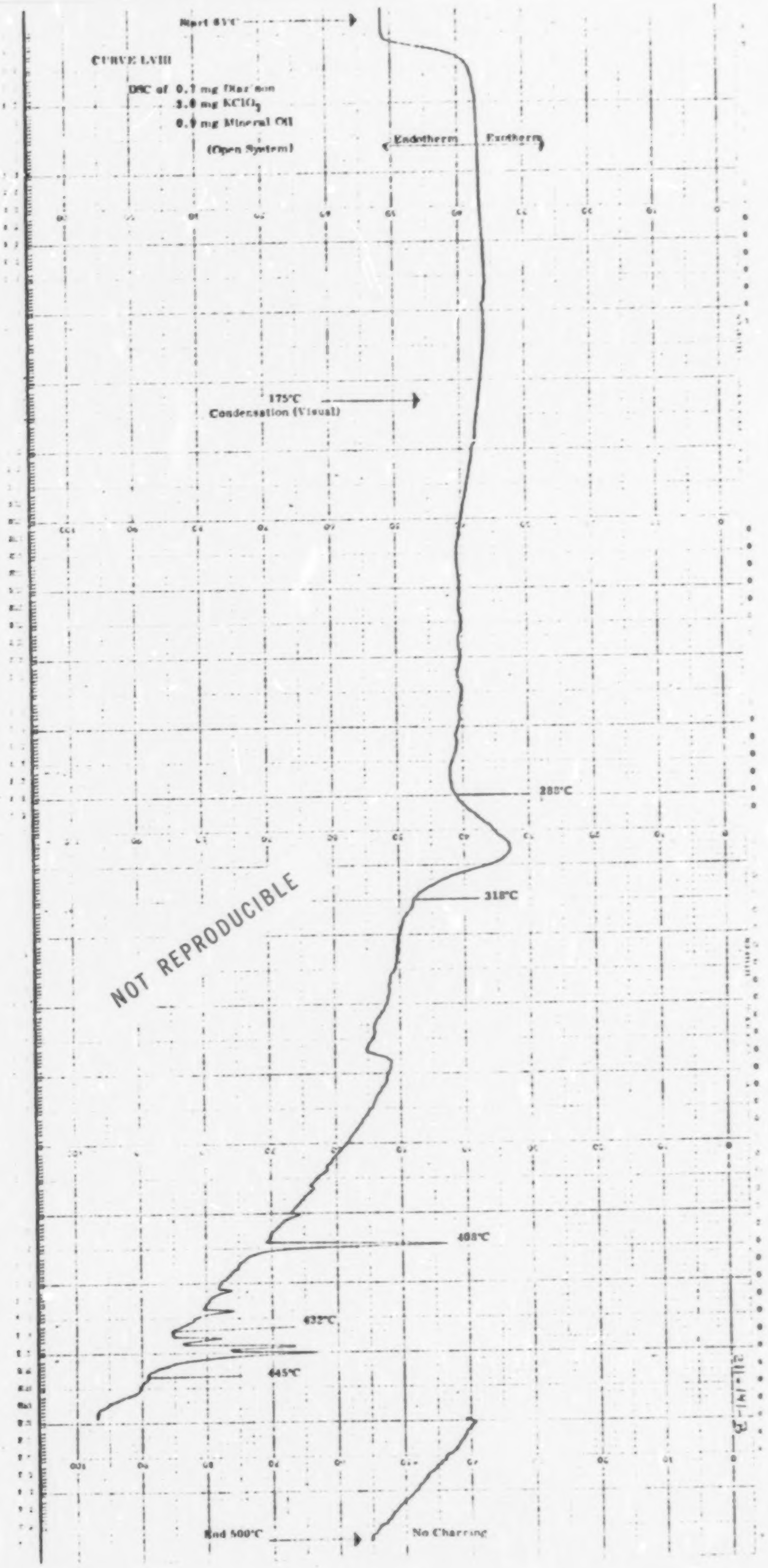

Start 65°C
CURVE LVI
DSC of 2.3 mg Dalapon
2.0 mg $KClO_3$
1.0 mg Mineral Oil
(Open System)
Endotherm
Exotherm
175°C
Condensation (Visual)
338°C
384°C
End 500°C
No Charring
21L-142-3



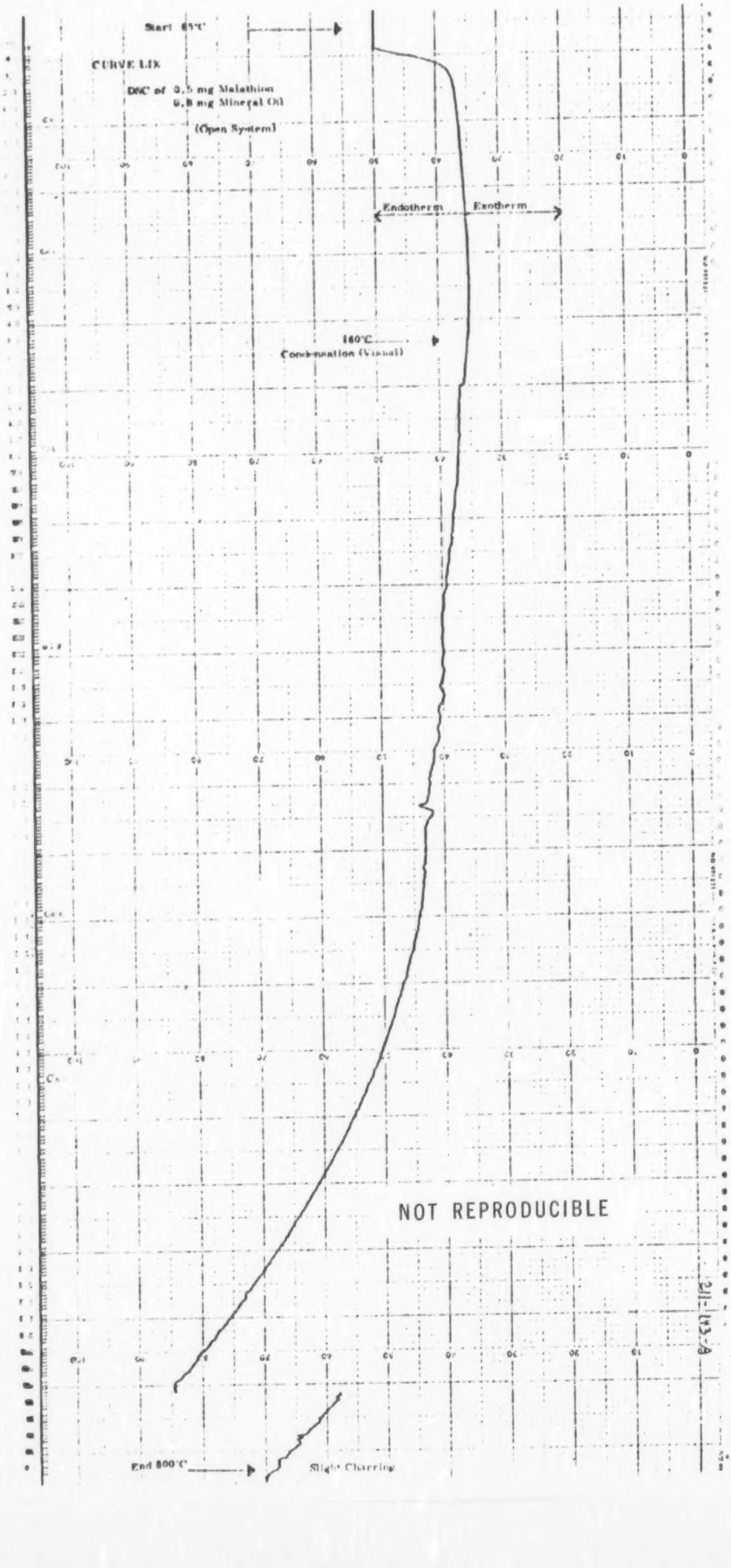
CURVE LVII

DSC of 0.7 mg Diazinon
0.8 mg Mineral Oil

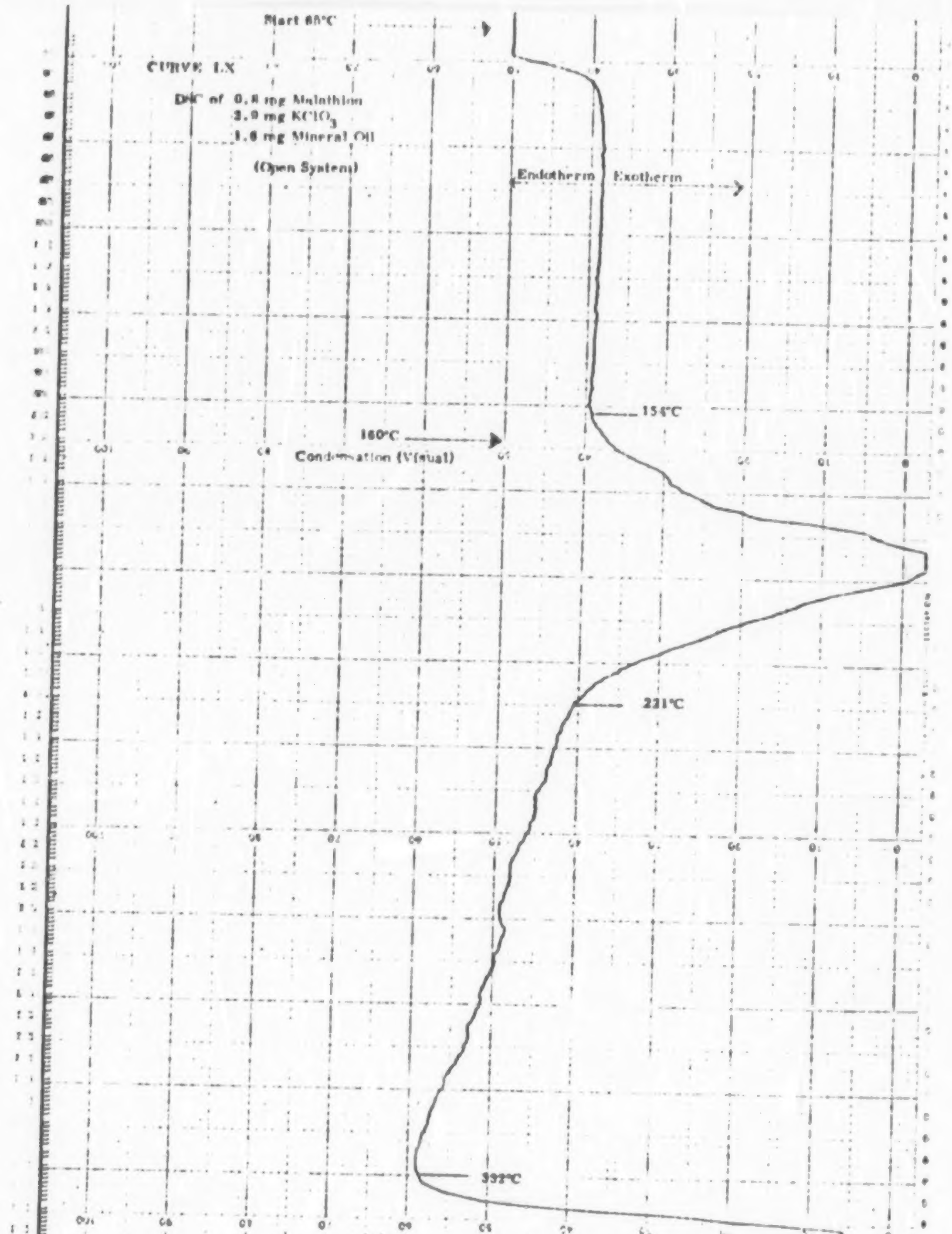
(Open System)

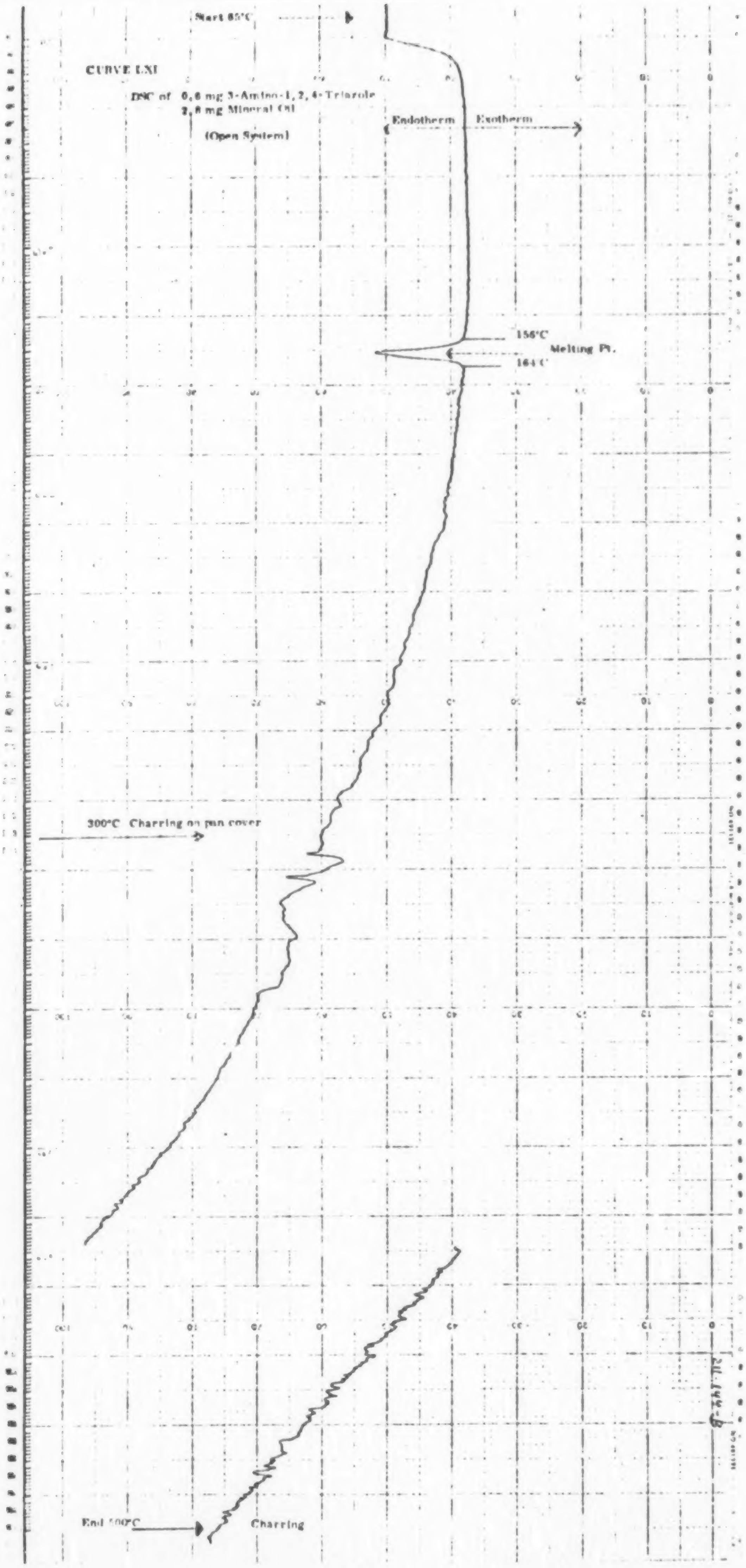


NOT REPRODUCIBLE



NOT REPRODUCIBLE

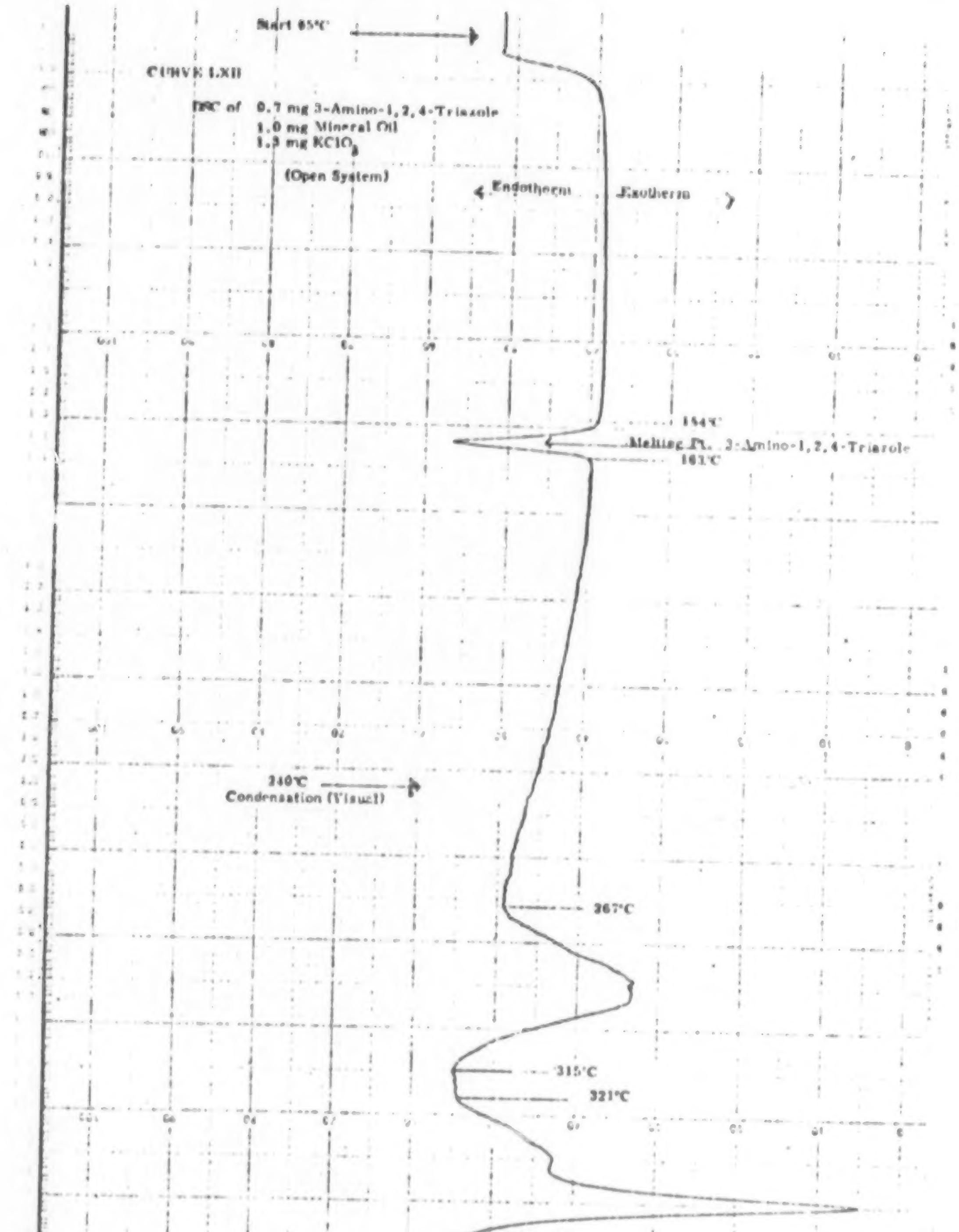

Start 65°C
CURVE LX
DTA of 0.8 mg Malathion
2.9 mg $KClO_3$
1.6 mg Mineral Oil
(Open System)
Endotherm Exotherm
154°C
160°C
Condensation (Visual)
221°C
332°C
382°C
211-143-B
End 500°C
Charring

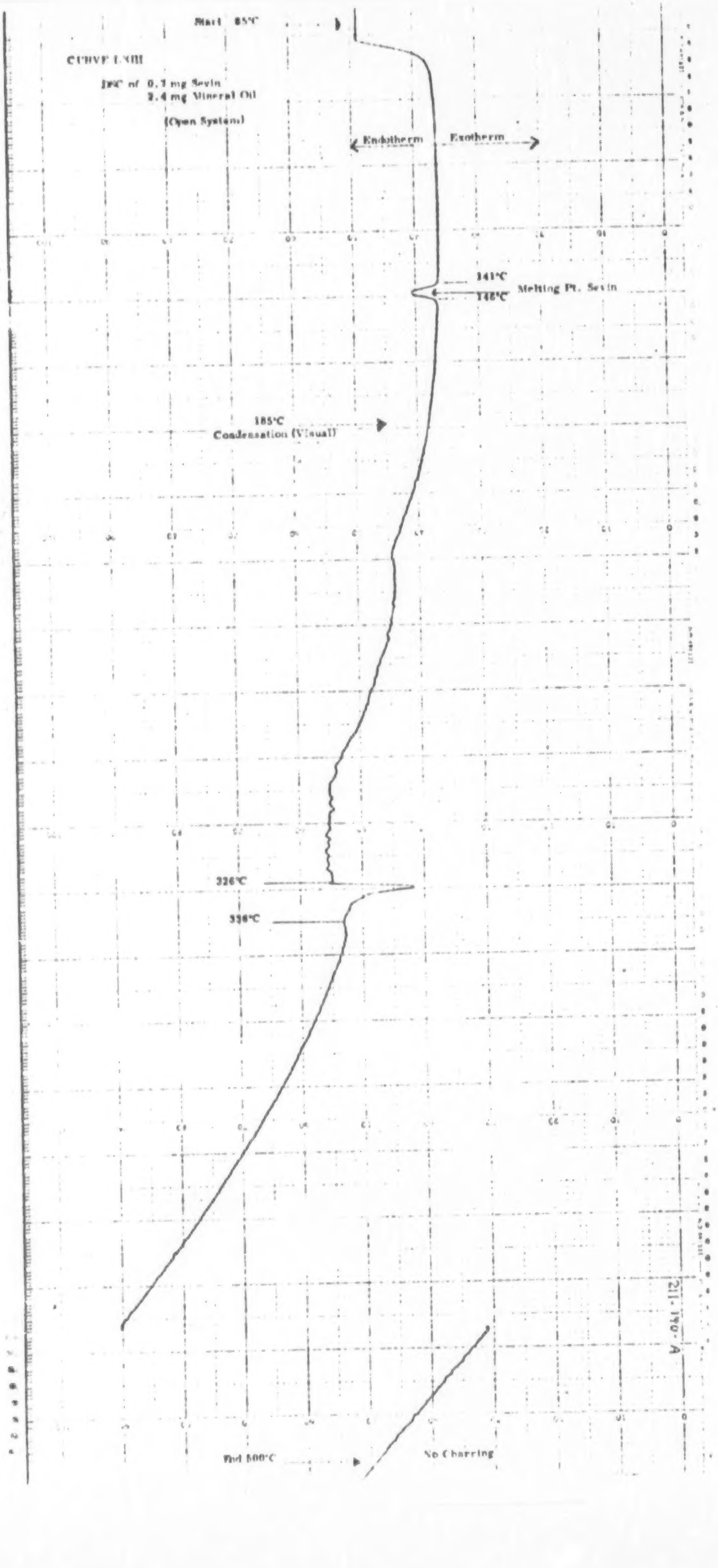


CURVE LXI

DSC of 0,6 mg 3-Amino-1, 2, 4-Triazole
2,8 mg Mineral Oil

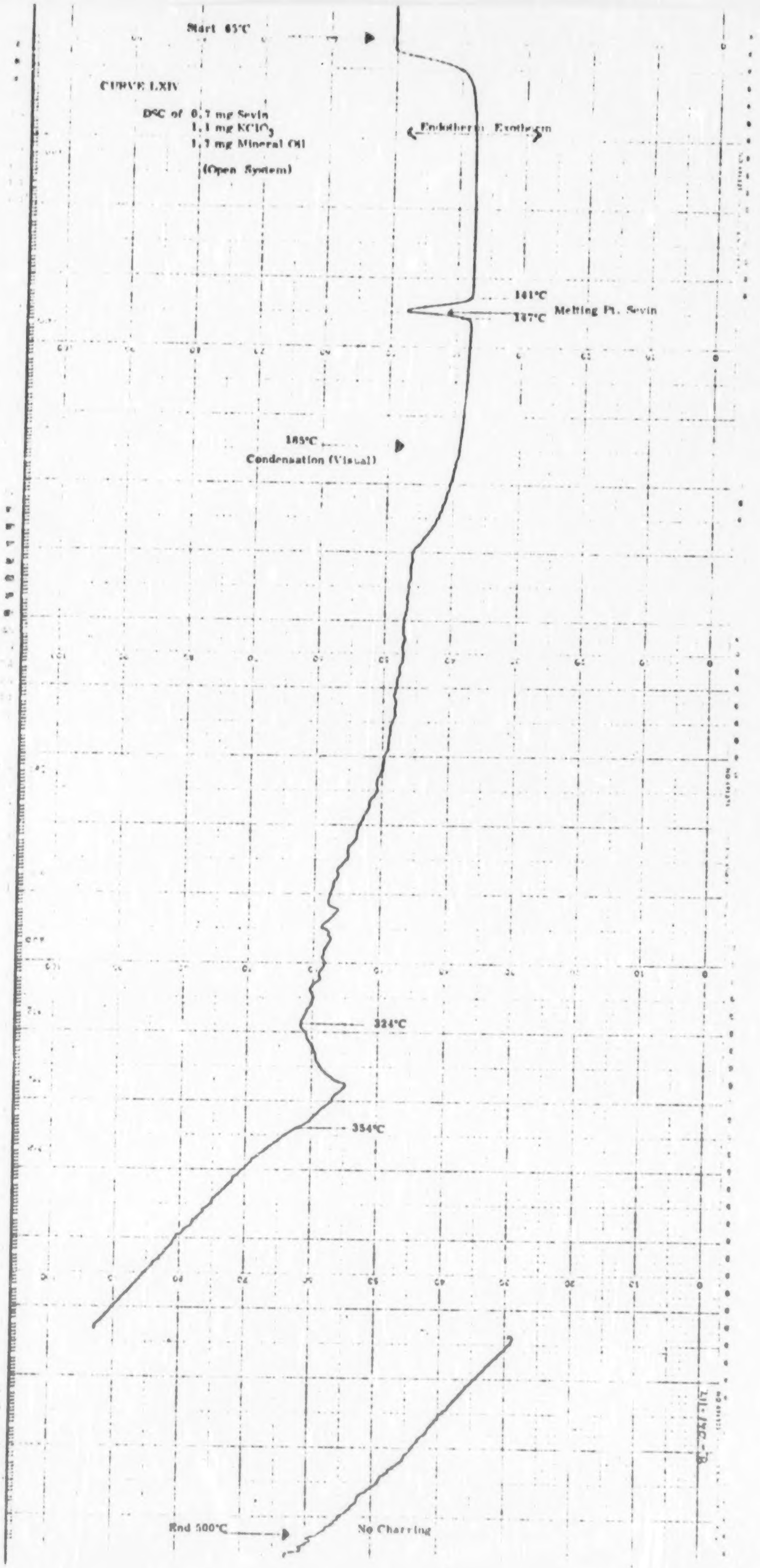
(Open System)

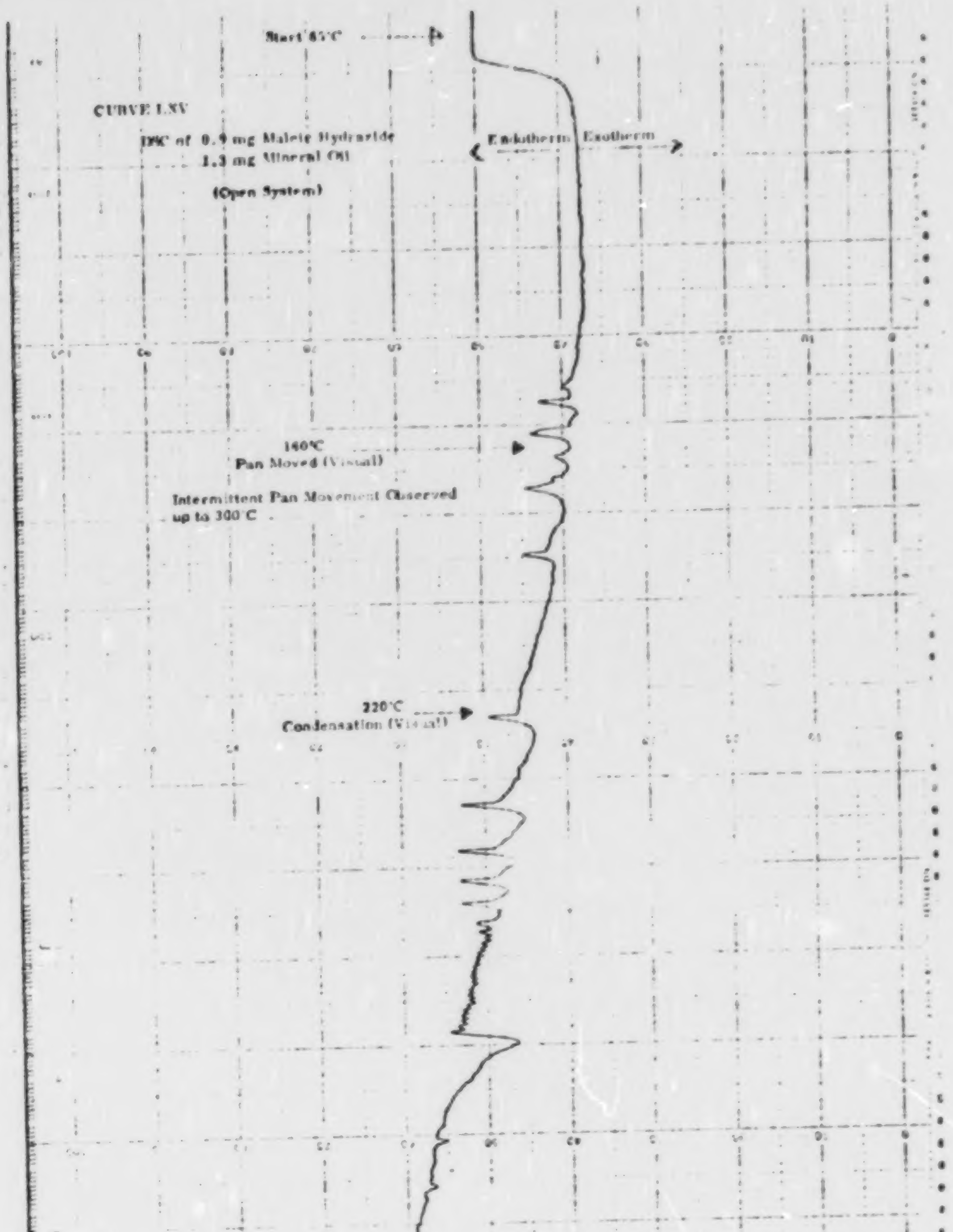

Start 65°C
CURVE LXII
DSC of 0.7 mg 3-Amino-1, 2, 4-Triazole
1.0 mg Mineral Oil
1.3 mg KClO3
(Open System)
Endotherm
Exotherm
154°C
Melting Pt. 3-Amino-1, 2, 4-Triazole
163°C
340°C
Condensation (Visual)
267°C
315°C
321°C
345°C
End 500°C
Charring
211-145-A


CURVE LXIII

DTA of 0.1 mg Sevin
2.4 mg Mineral Oil

(Open System)

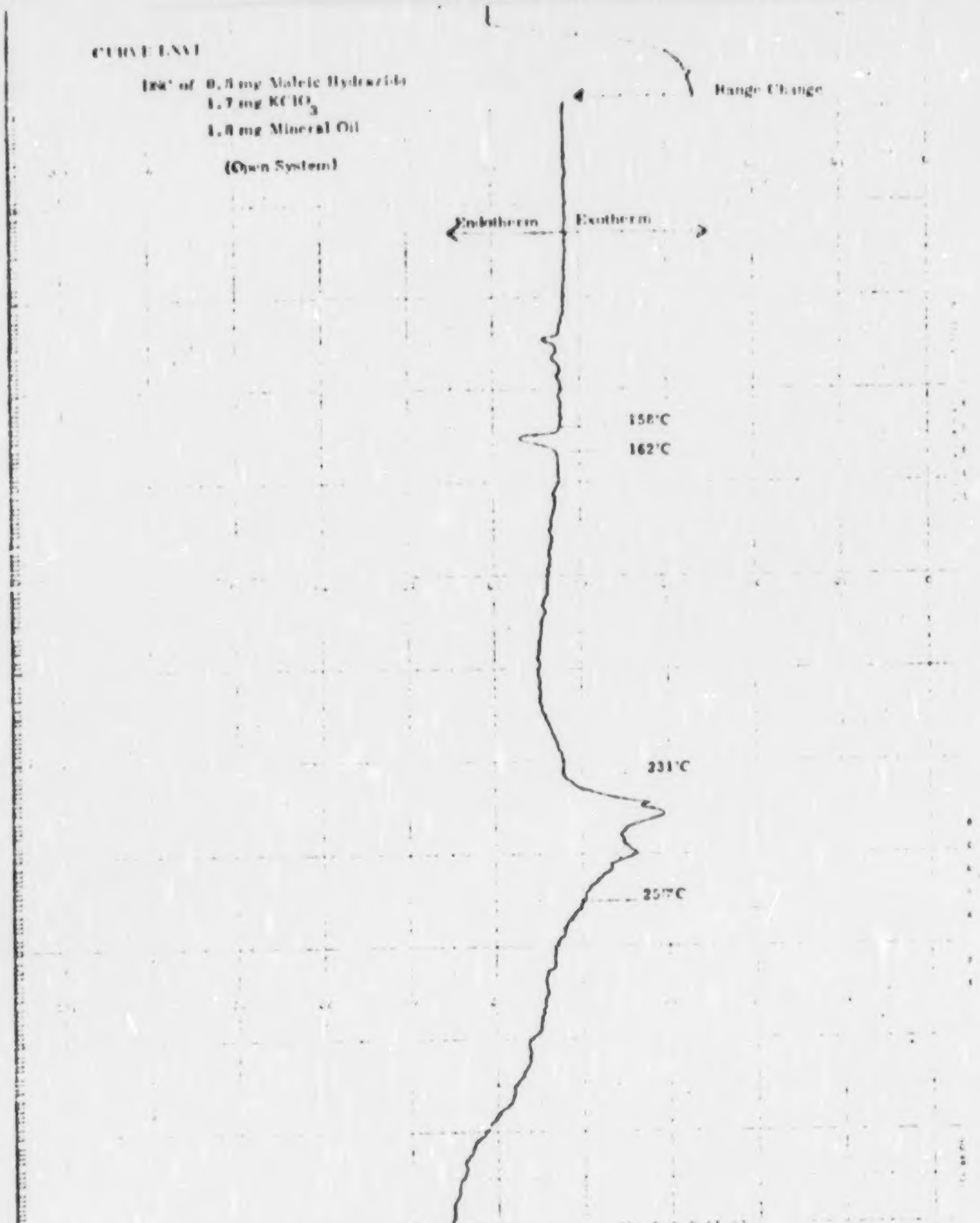

Start 65°C
CURVE LXIV
DSC of 0.7 mg Sevin
1.1 mg KClO$_3$
1.7 mg Mineral Oil
(Open System)
Endotherm Exotherm
141°C
147°C
Melting Pt. Sevin
185°C
Condensation (Visual)
324°C
354°C
End 500°C
No Charring



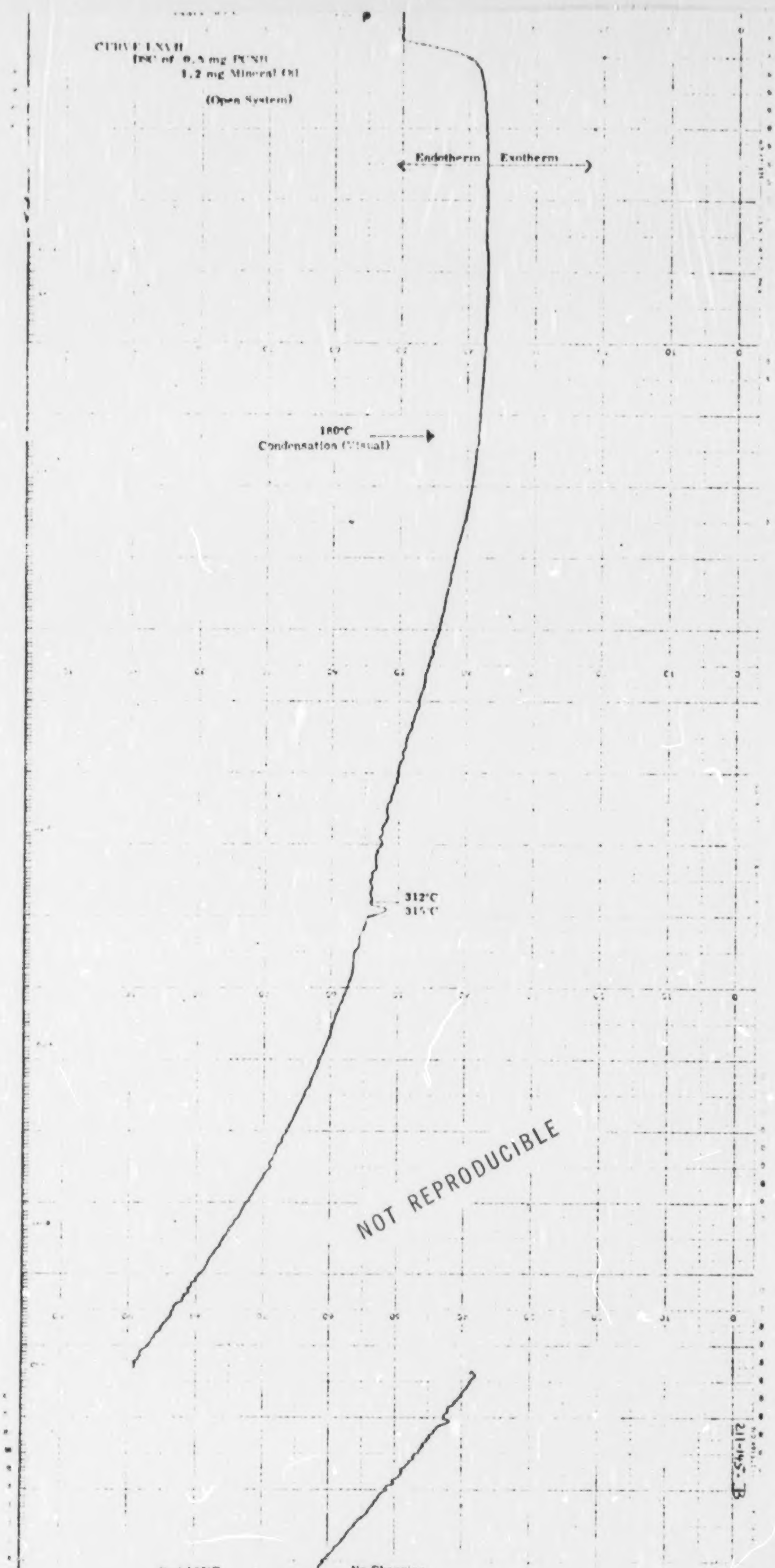
CURVE LXV

DSC of 0.9 mg Maleic Hydrazide
1.3 mg Mineral Oil

(Open System)



NOT REPRODUCIBLE

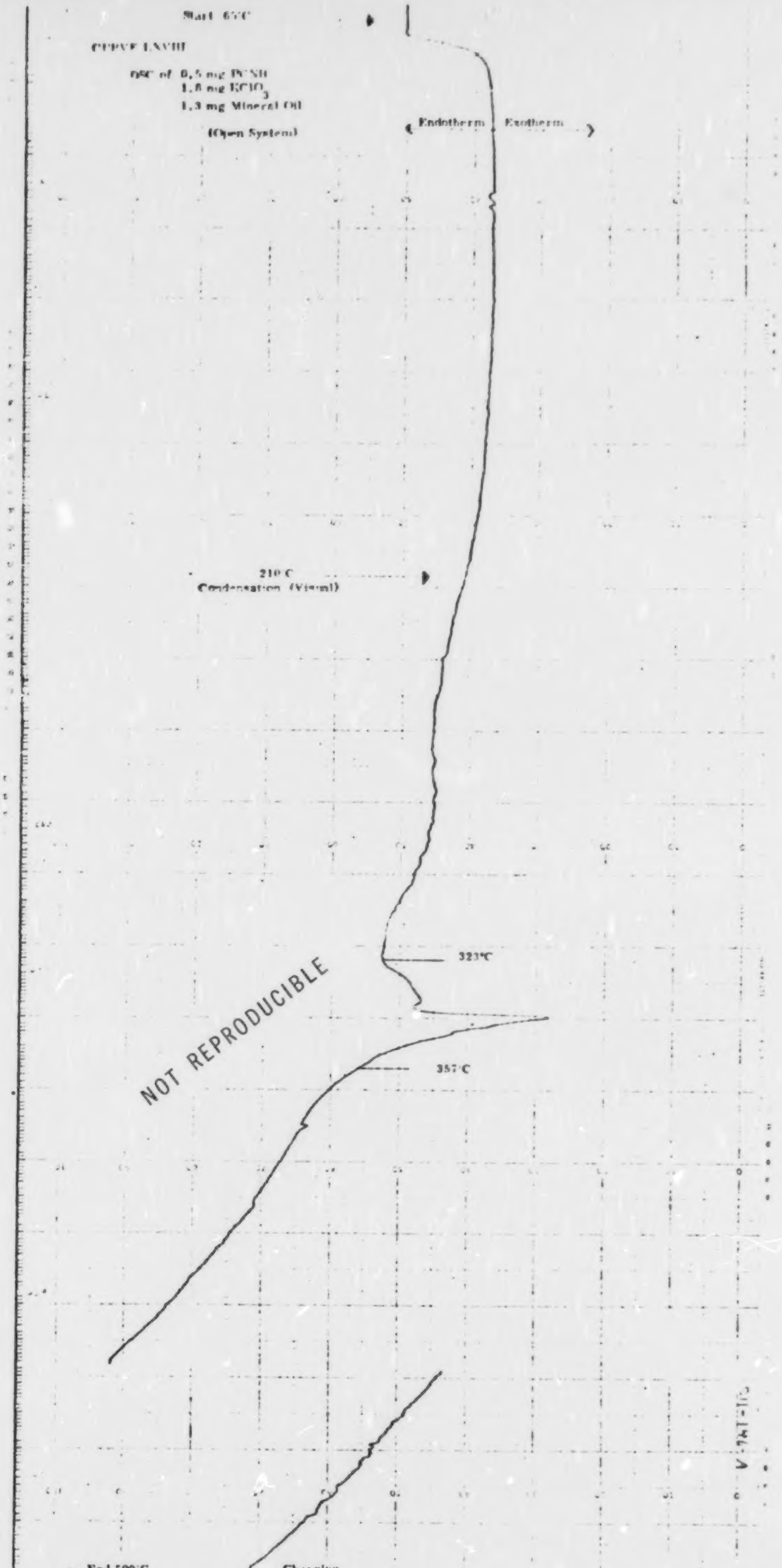


NOT REPRODUCIBLE

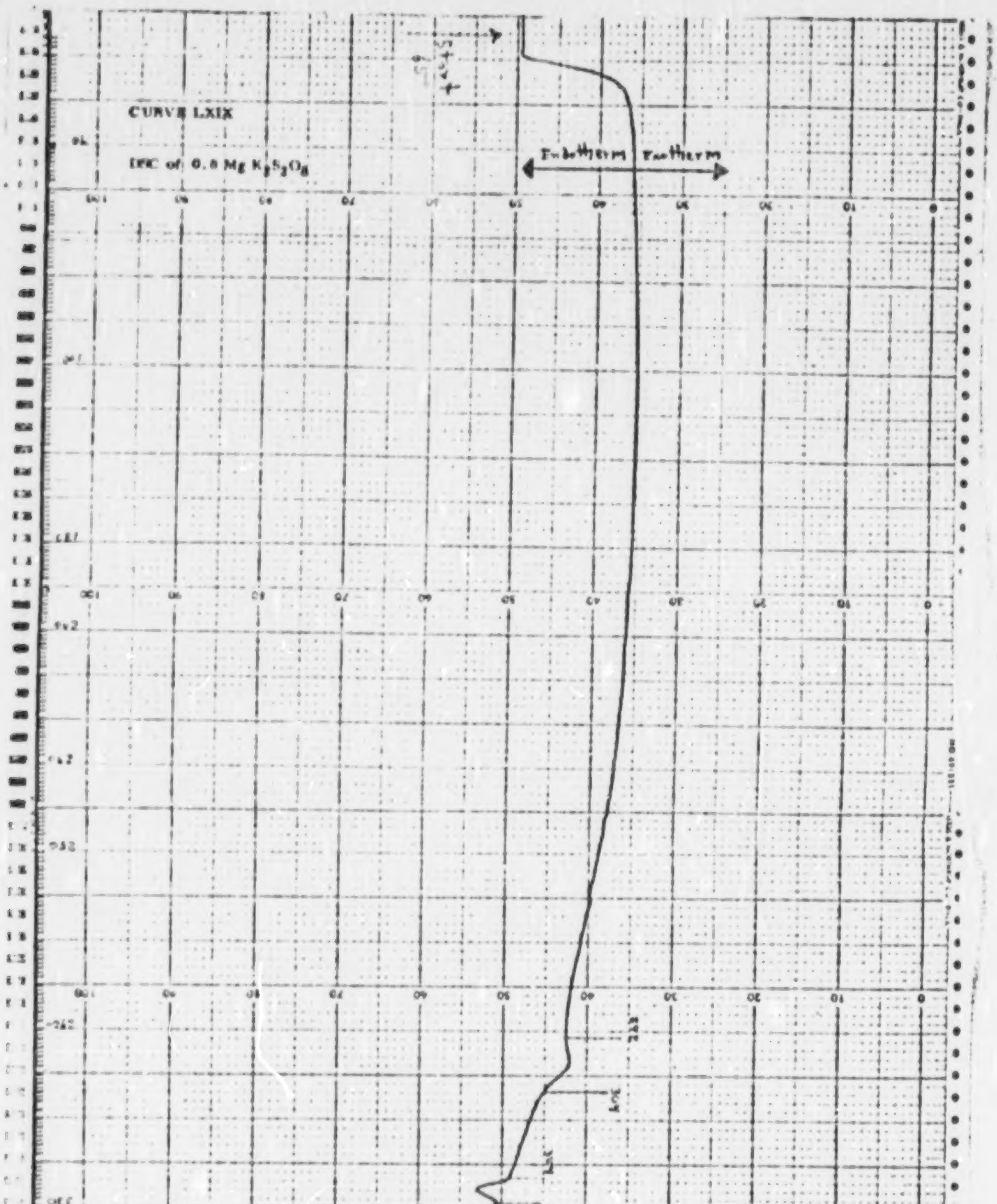
CURVE LXVIII

DSC of 0.5 mg PCNB
1.8 mg $KClO_3$
1.3 mg Mineral Oil

(Open System)

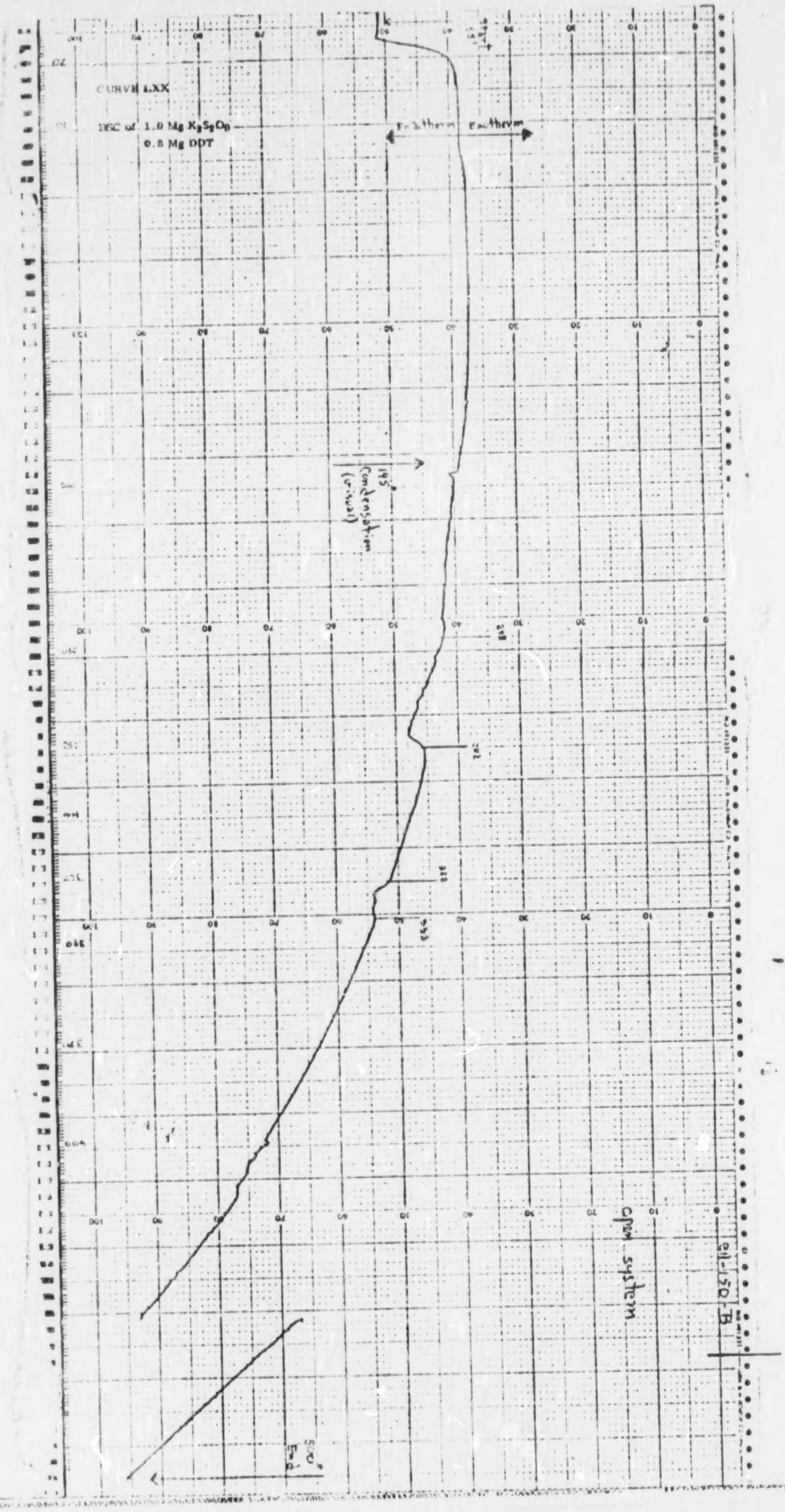


NOT REPRODUCIBLE



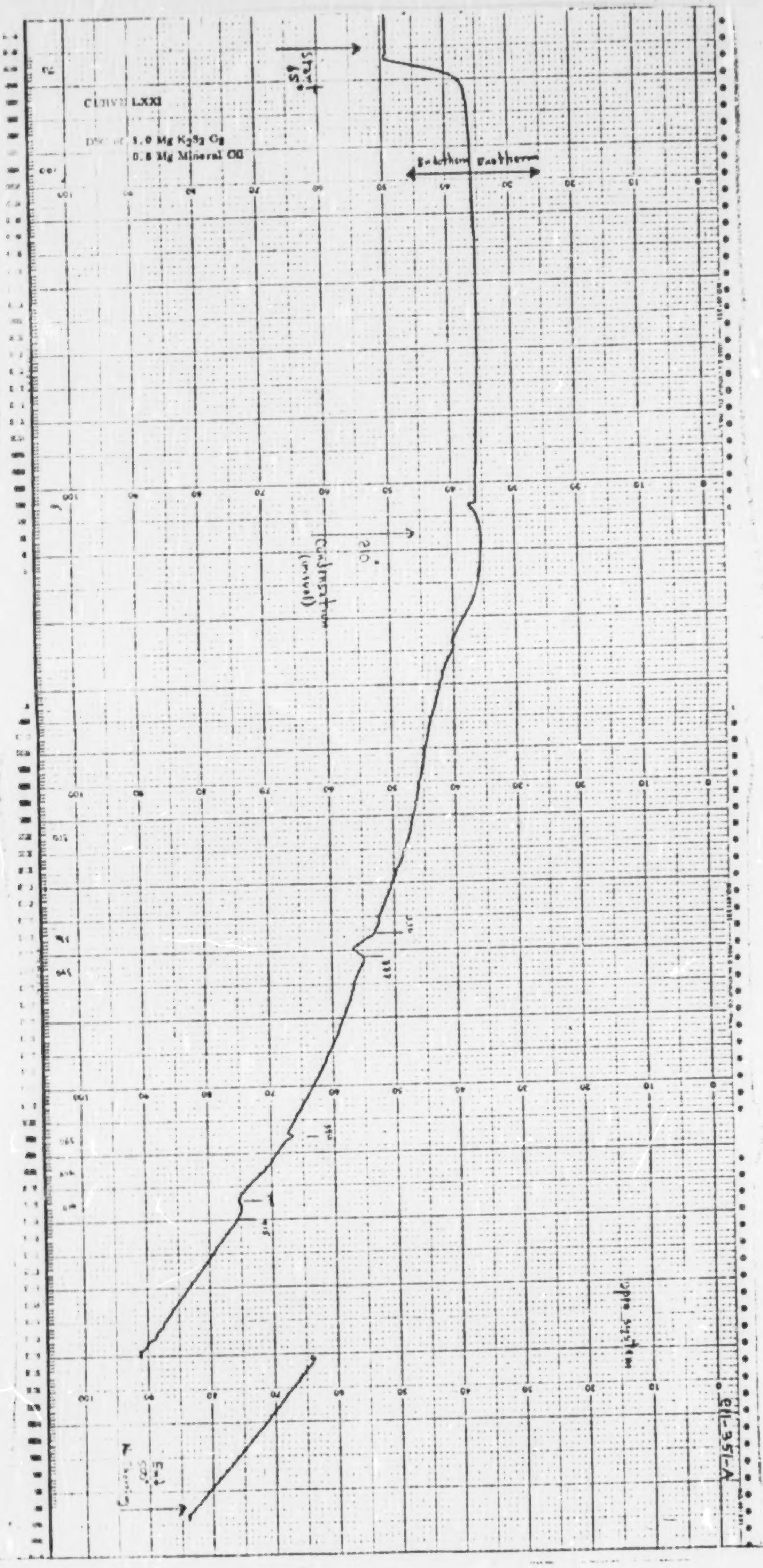
CURVE LXIX

DTC of 0.8 Mg $K_2S_2O_8$

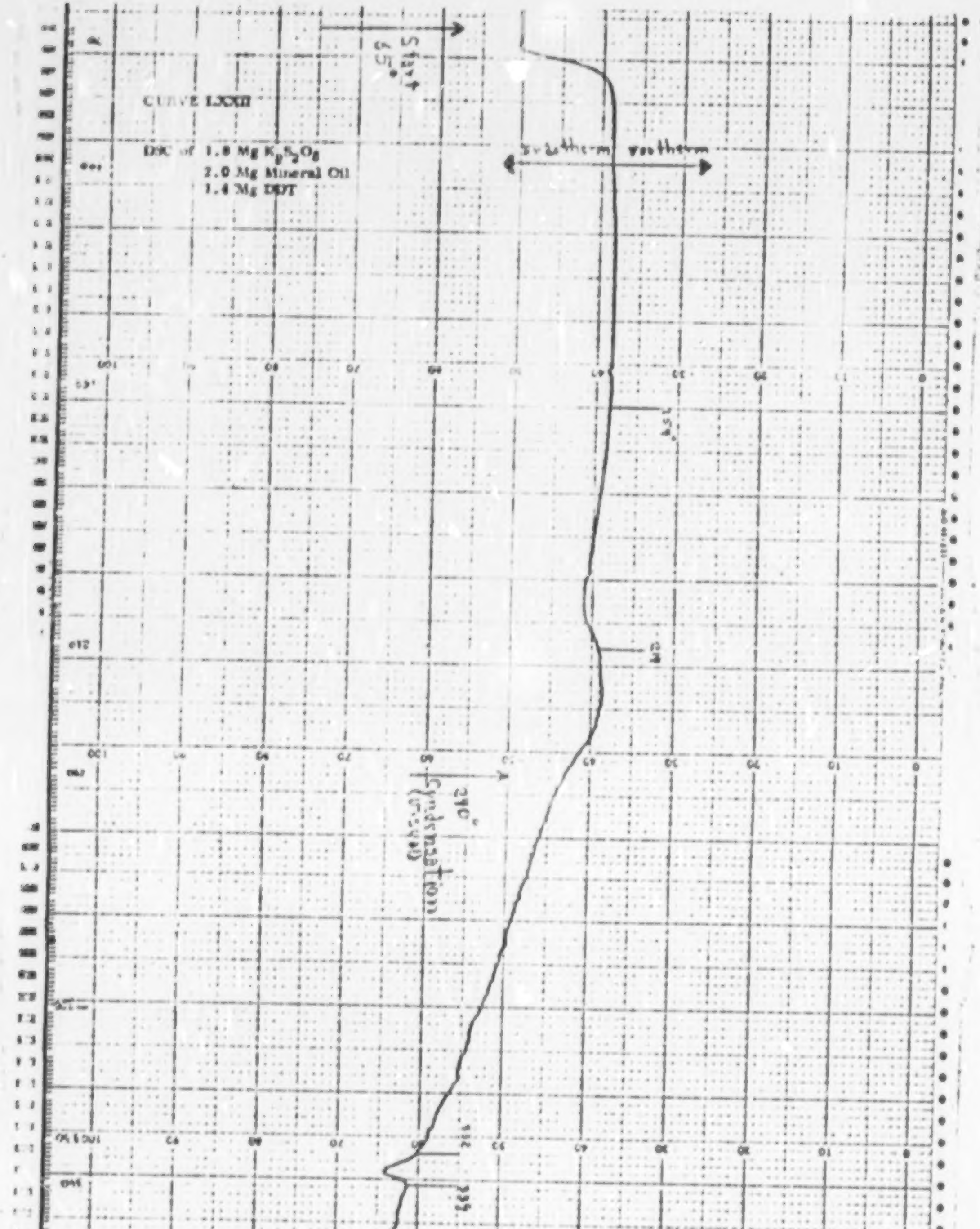


CURVE LXX

DSC of 1.0 Mg $K_2S_2O_8$
0.8 Mg DDT

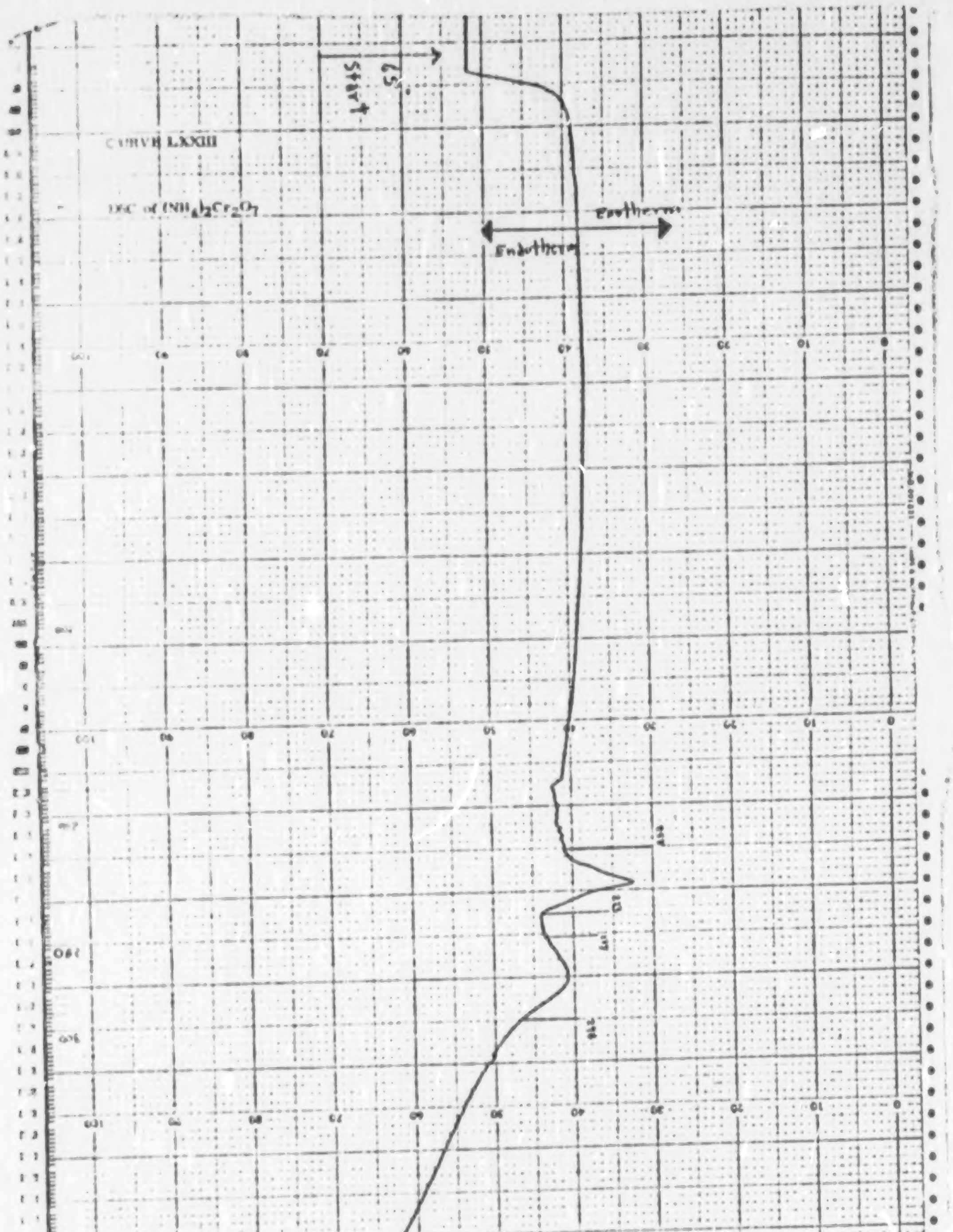


CURVE LXXI
DSC of 1.0 Mg $K_2S_2O_8$
0.5 Mg Mineral Oil
Start 59°
Endotherm Exotherm
Sublimation (partial)
210°
open system
End 325°
511-351-A

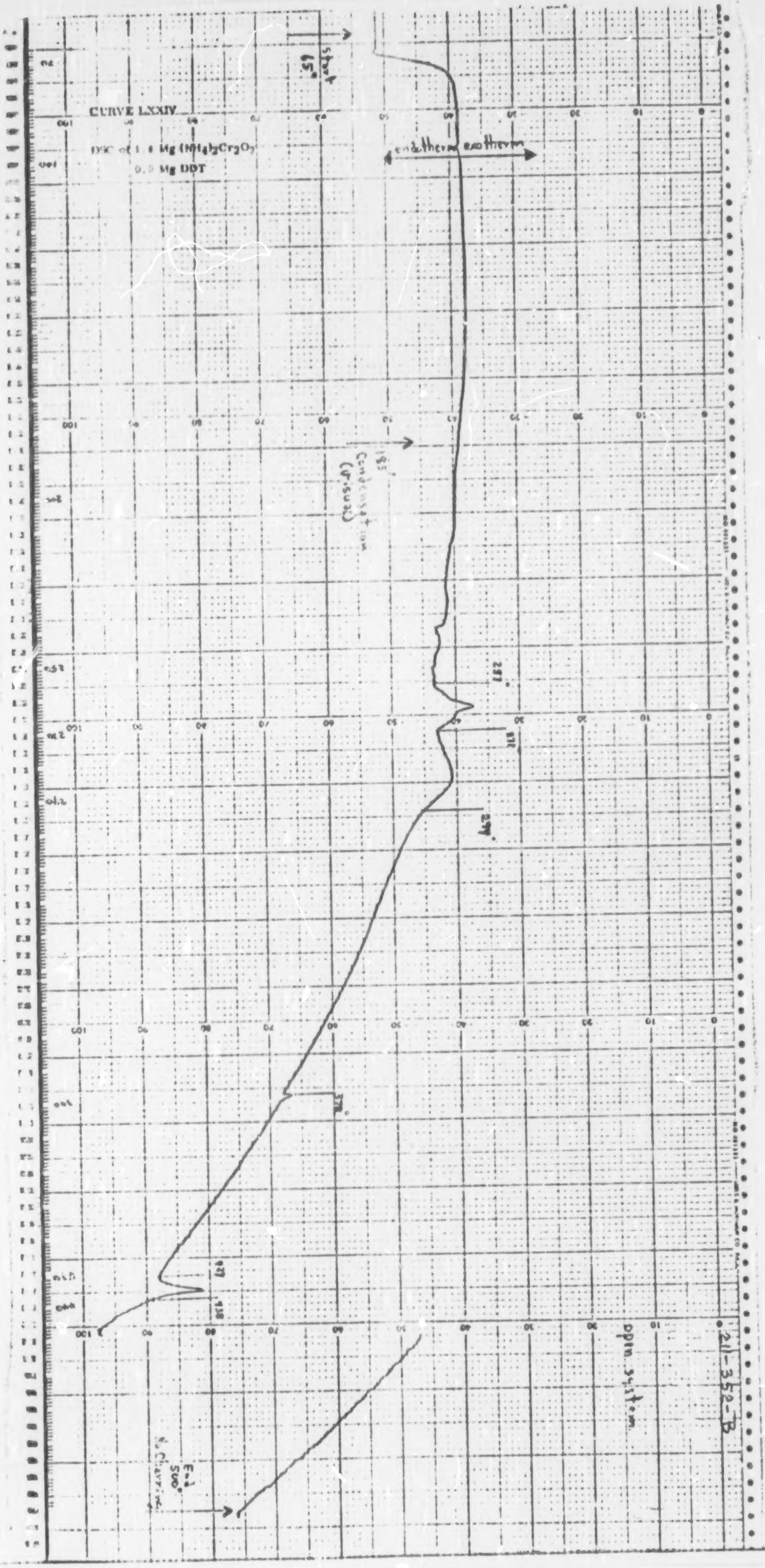


CURVE LXXII

DSC of 1.8 Mg $K_2S_2O_8$
2.0 Mg Mineral Oil
1.4 Mg DDT


CURVE LXXIII

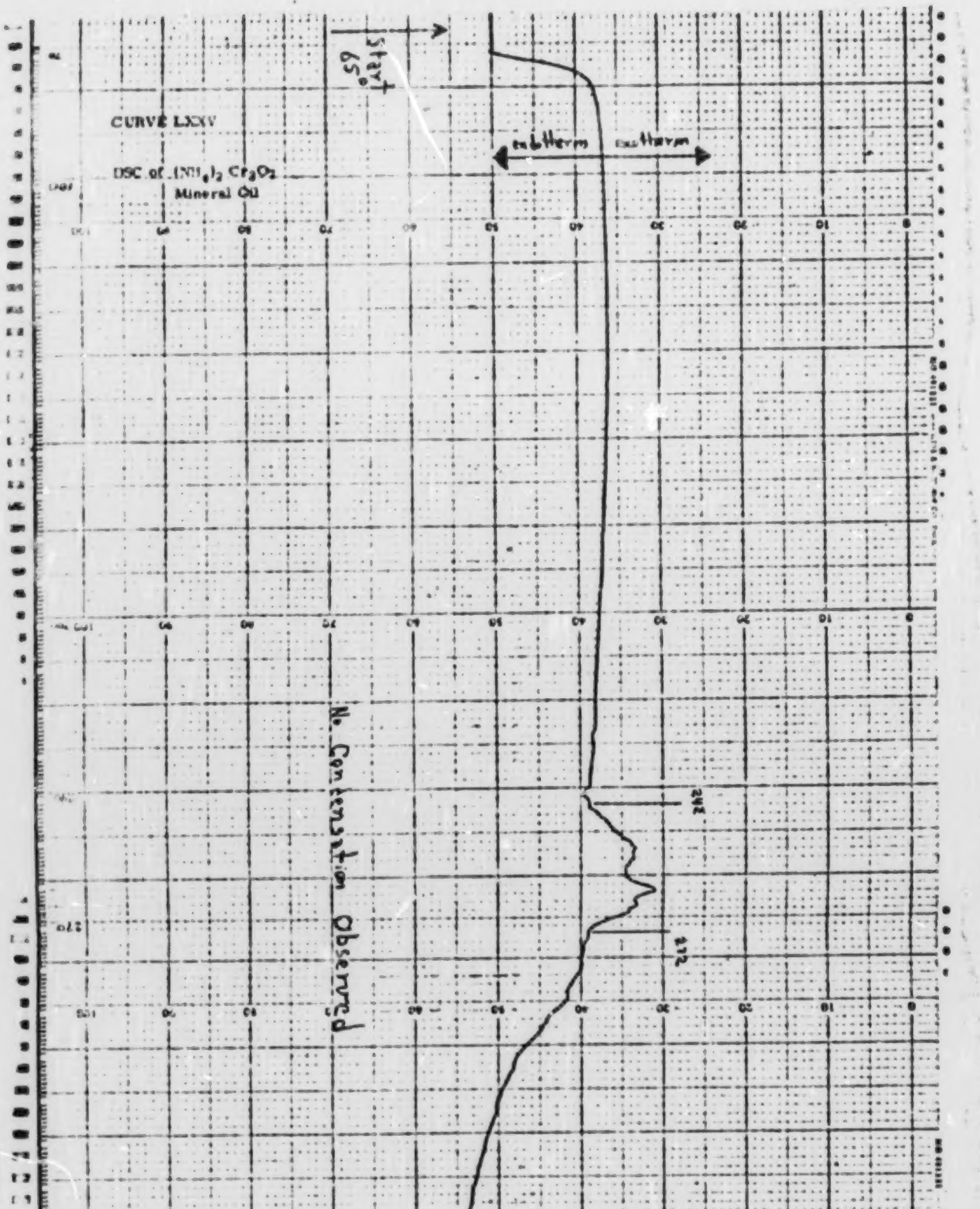
DSC of $(NH_4)_2Cr_2O_7$

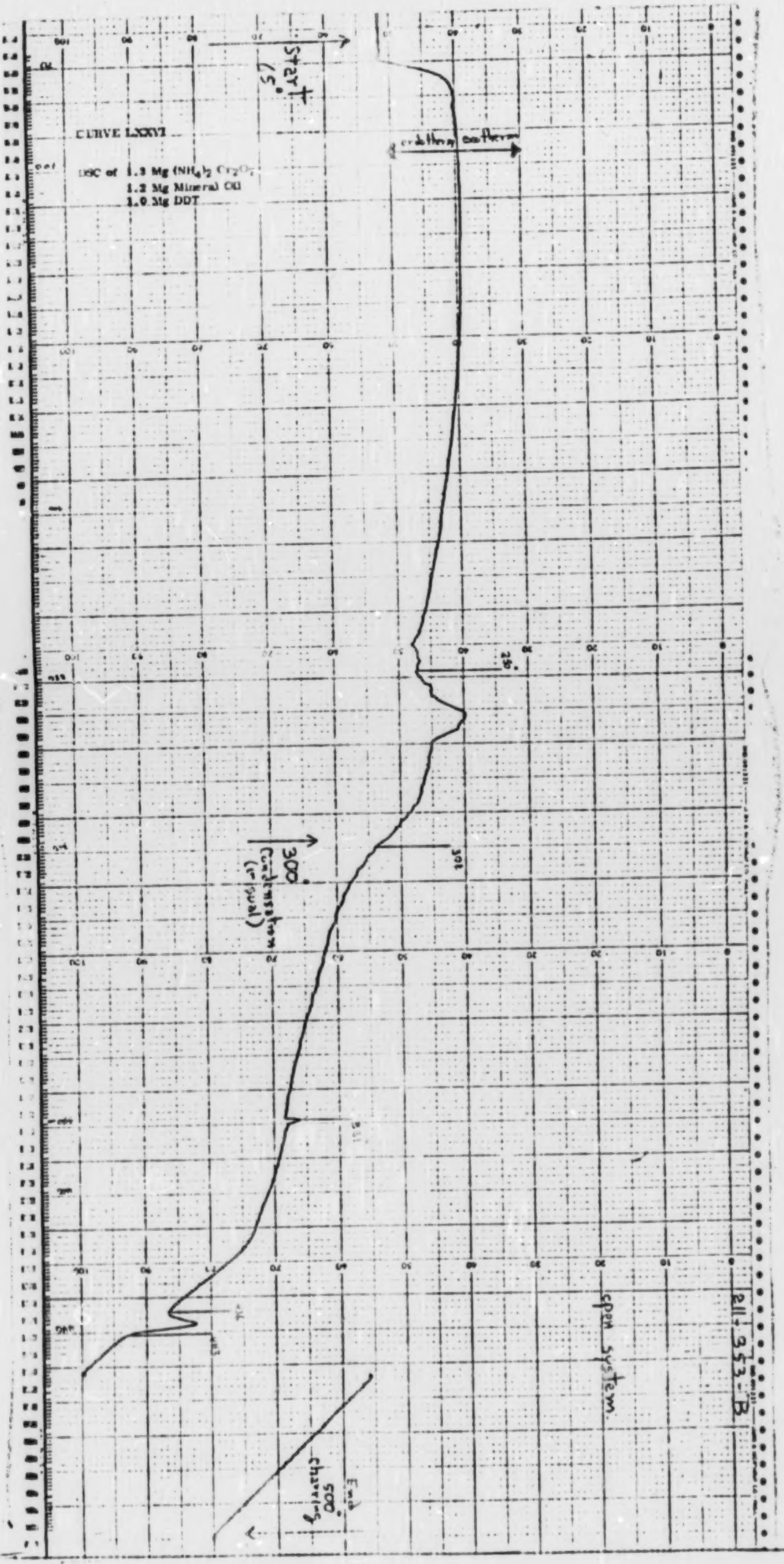


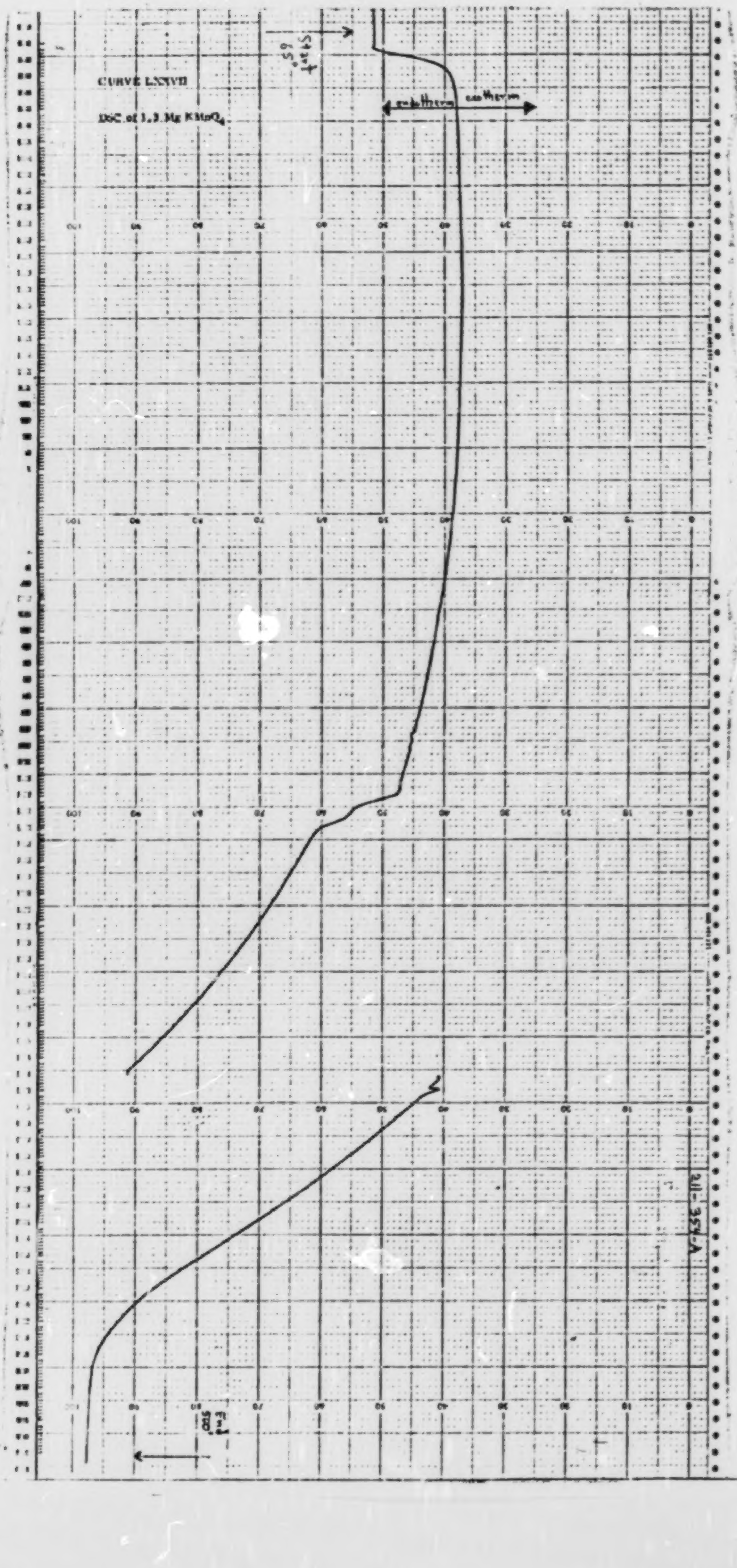
CURVE LXXIV

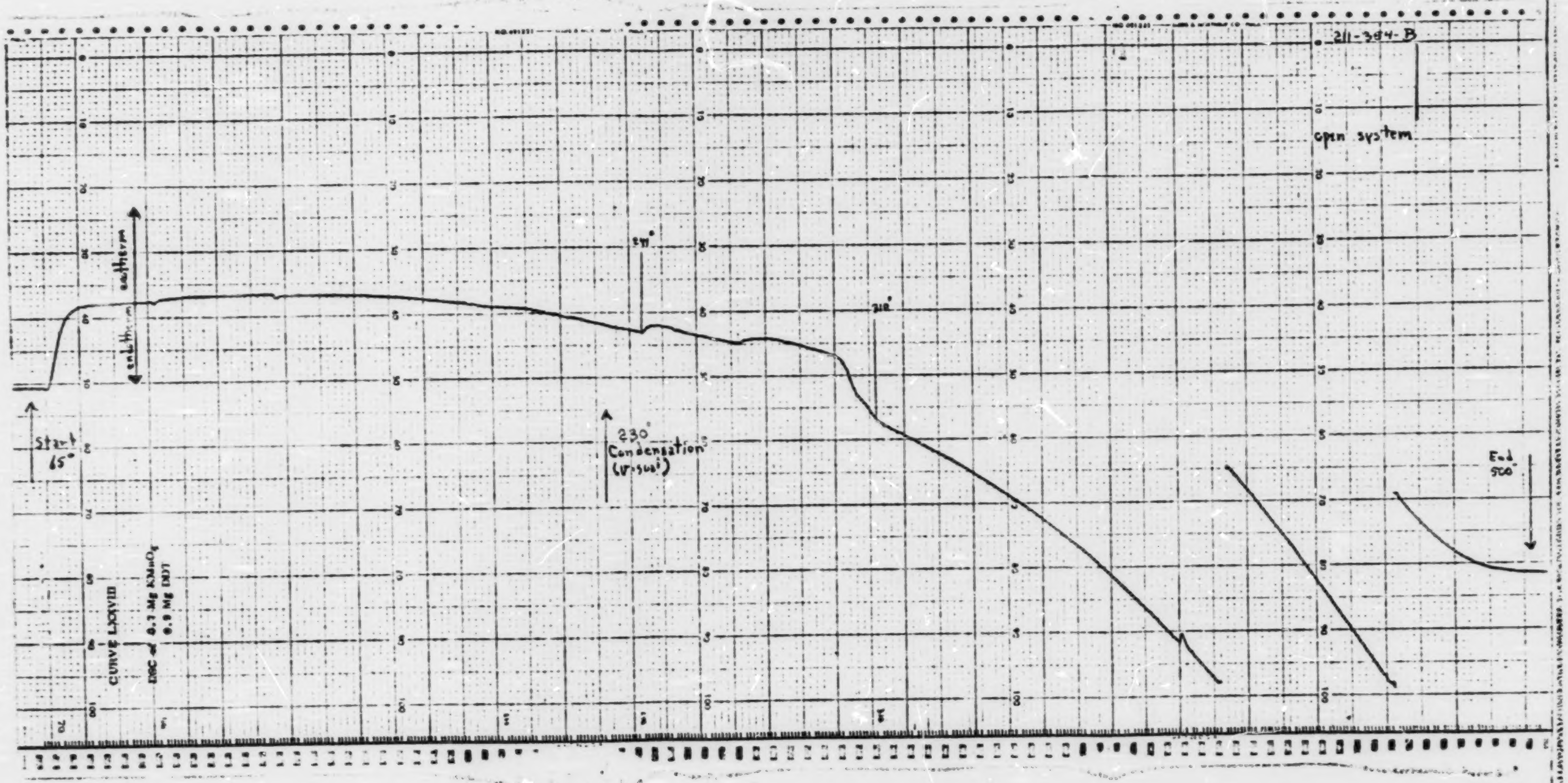
DSC of 1.0 Mg $(NH_4)_2Cr_2O_7$

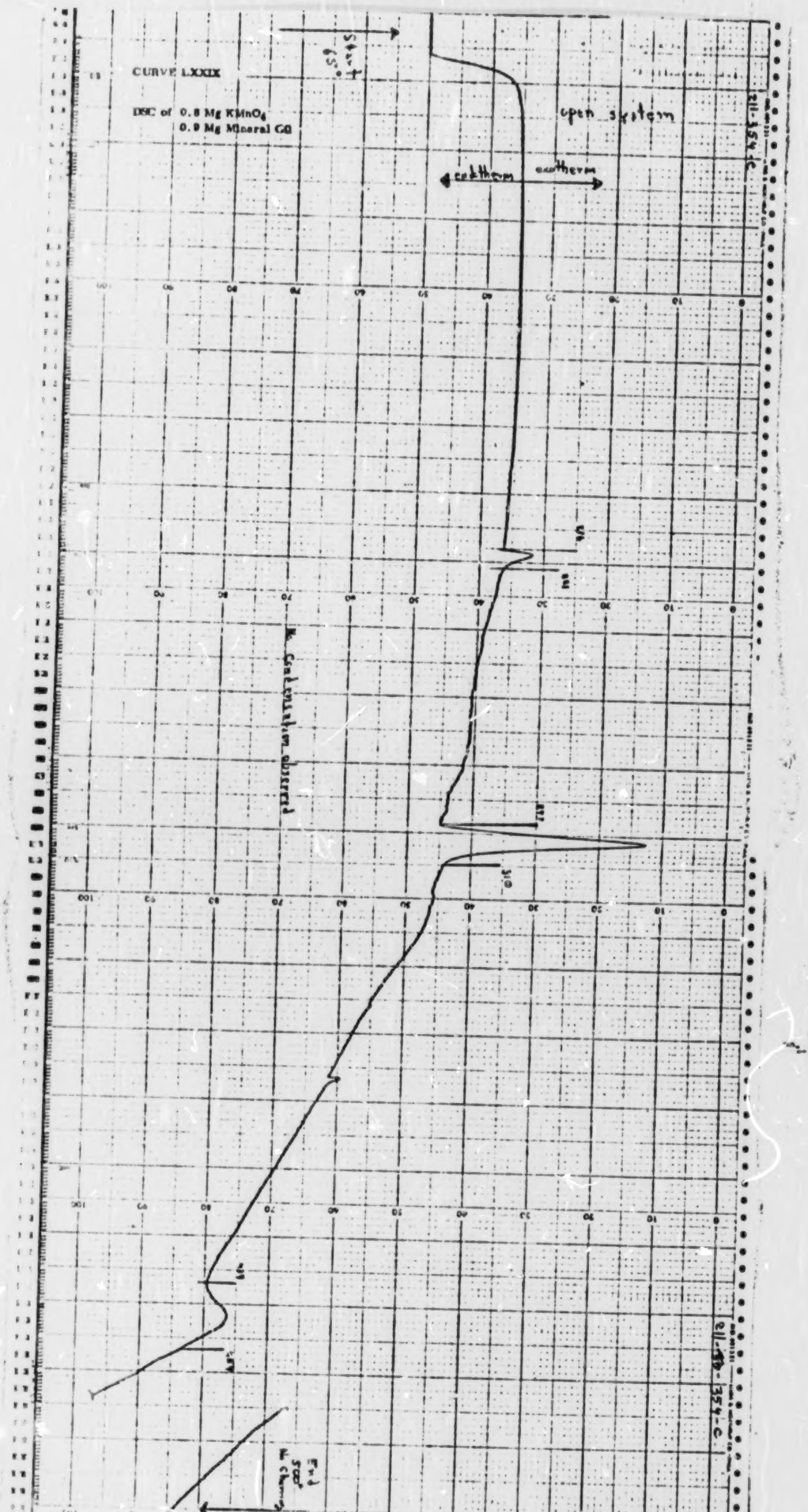
0.5 Mg DDT


CURVE LXXV
DSC of $(NH_4)_2Cr_2O_7$
Mineral Oil
Start
65°
endotherm
exotherm
No Condensation Observed
242
272
End
600°
Charring
open system
211-35b-A


CURVE LXXVI
DSC of 1.3 Mg (NH4)2 Cr2O7
1.2 Mg Mineral Oil
1.0 Mg DDT
Start 25°
oxidation isotherm
250
300° Condensation (visual)
301
381
436
463
open system
End 500° charring
211-353-B

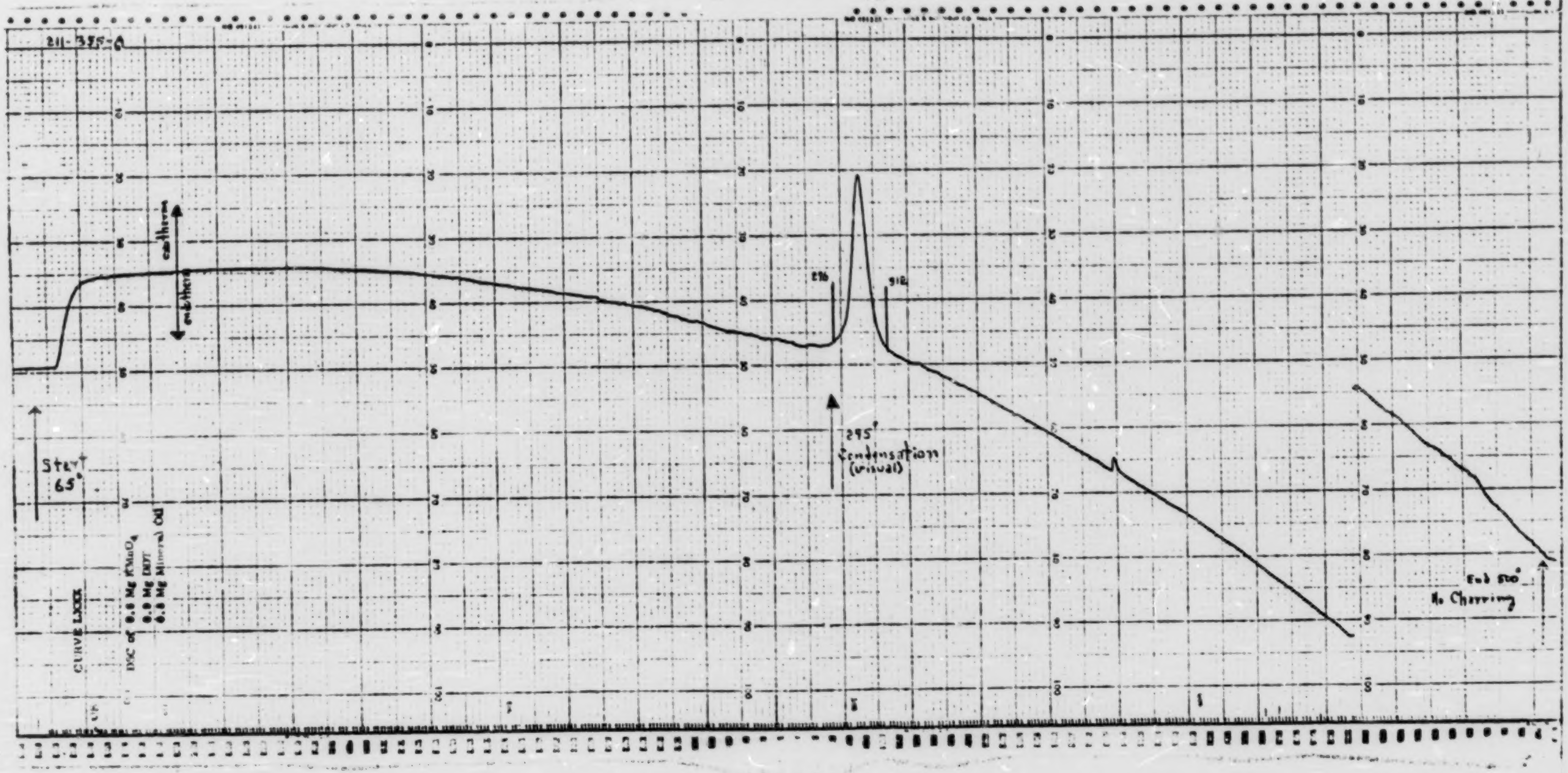

CURVE LXXVII
DSC of 1.3 Mg KMnO$_4$
Start 65°
endotherm
exotherm
End 500°
211-354-A
100
90
80
70
60
50
40
30
20
10
0

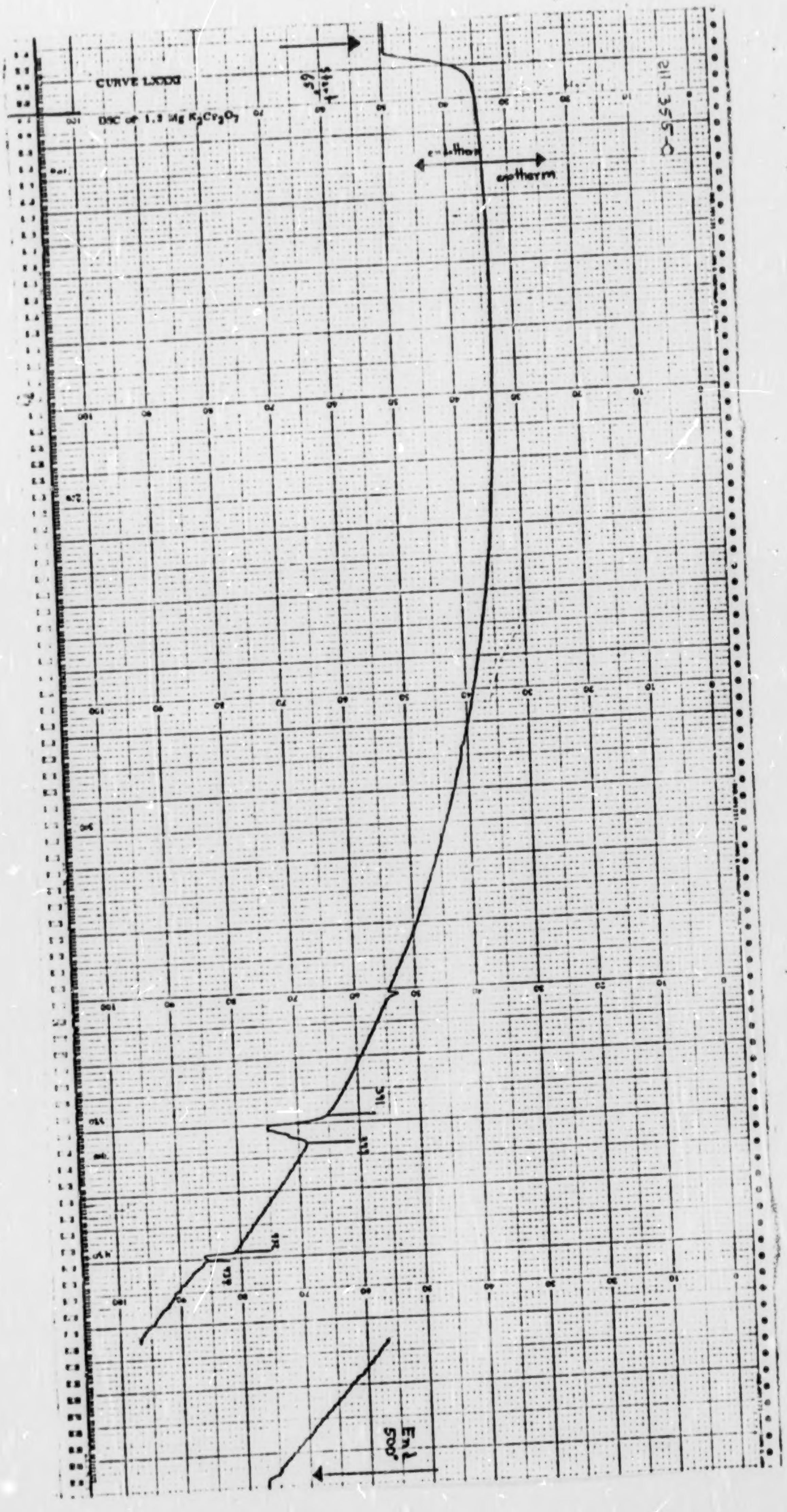

CURVE LXXVIII
DSC of 0.7 Mg $KMnO_4$
0.9 Mg DDT
Start 65°
endotherm
exotherm
230° Condensation (visual)
277°
318°
open system
End 500°
211-384-B

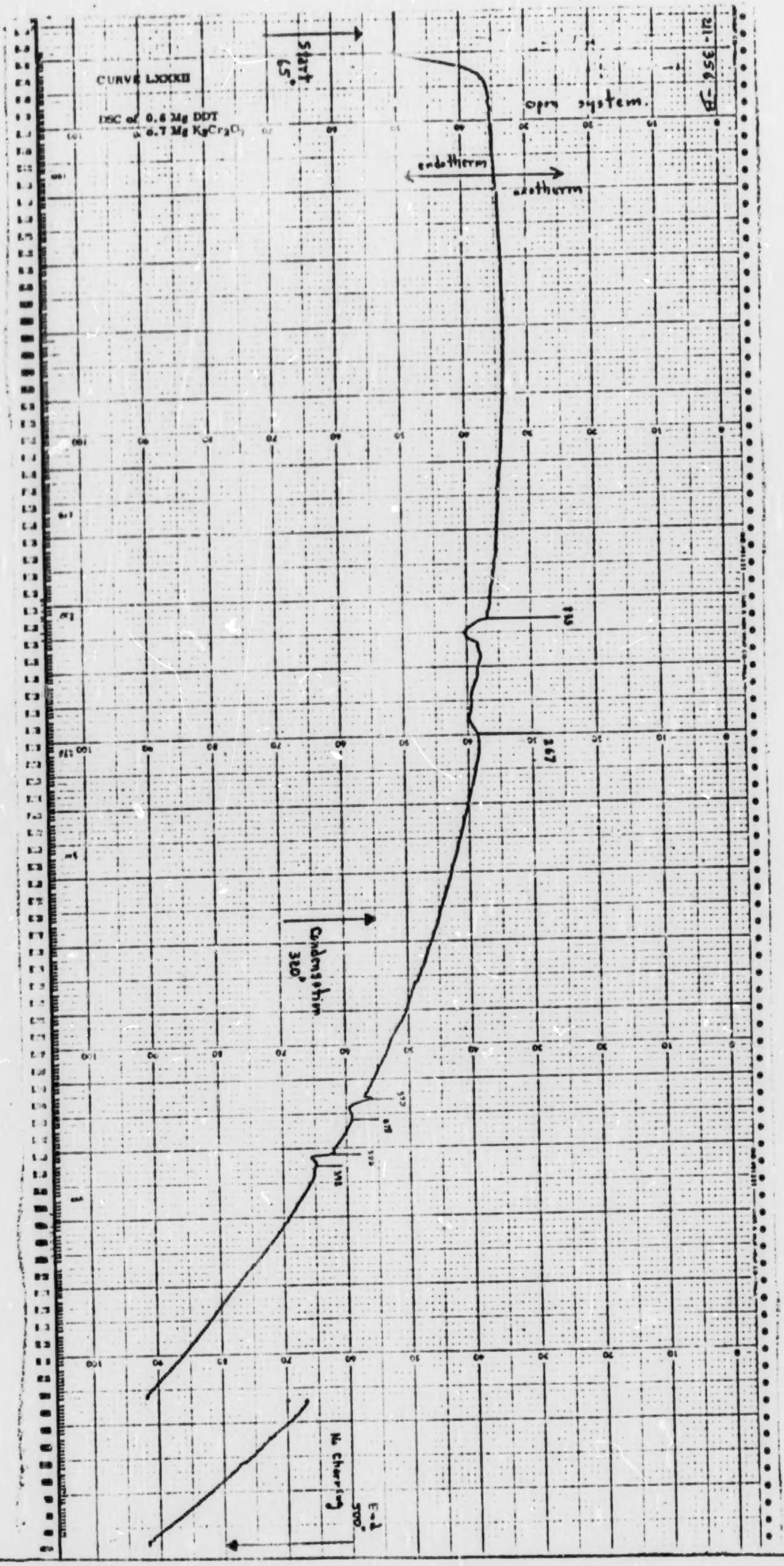


CURVE LXXIX

DSC of 0.8 Mg $KMnO_4$
0.9 Mg Mineral G0

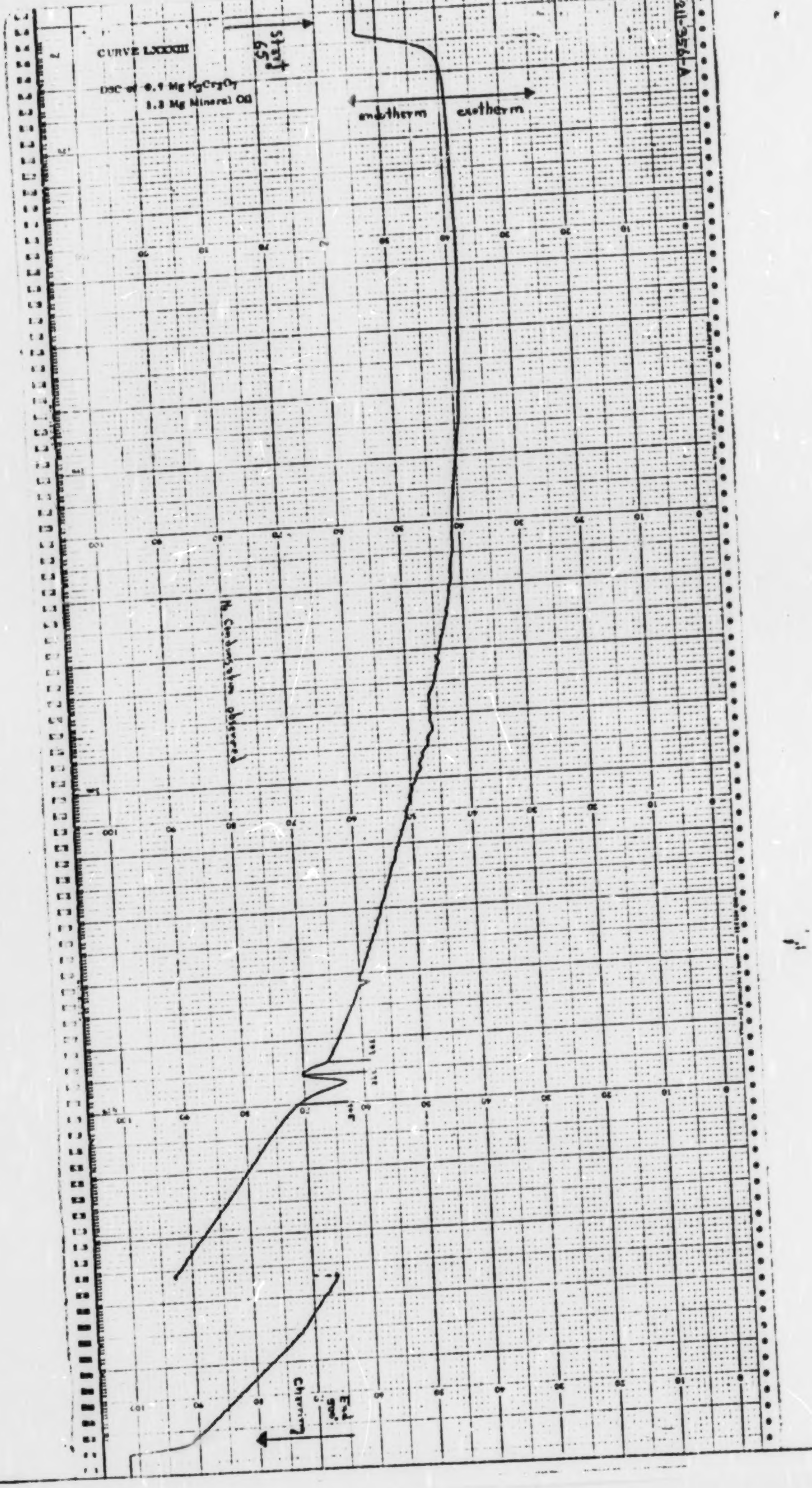

211-335-Q
CURVE LXXX
DSC of 0.8 Mg KMnO4
0.9 Mg DDT
0.8 Mg Mineral Oil
Start 65°
exotherm
endotherm
286
316
295° Condensation (visual)
End 500° to Charring
0
10
20
30
40
50
60
70
80
90
100

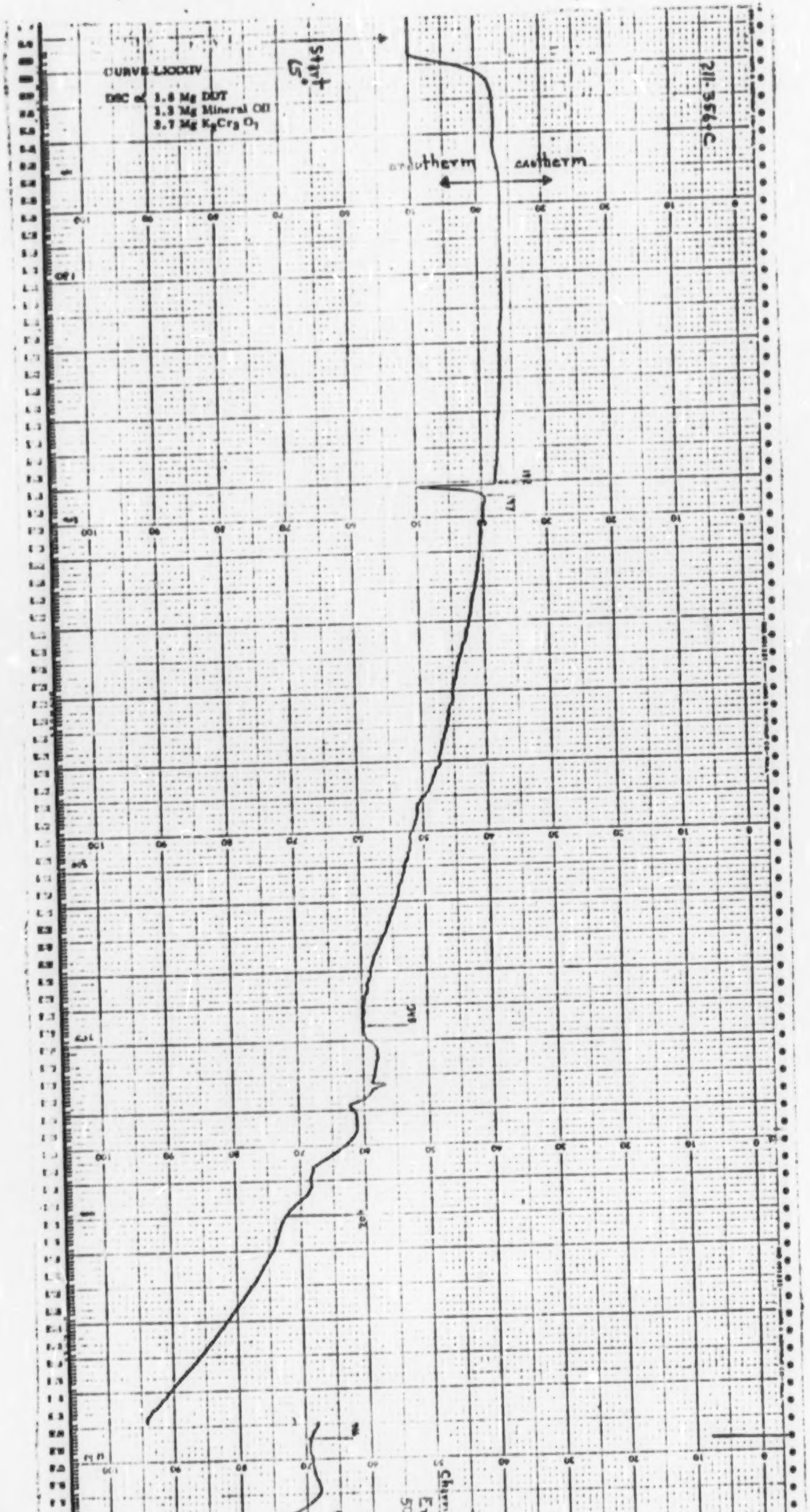

CURVE LXXXI
DSC of 1.3 Mg K₂Cr₂O₇
Start 65°
endotherm
exotherm
311-355-C
391
399
412
409
End 500°



CURVE LXXXII

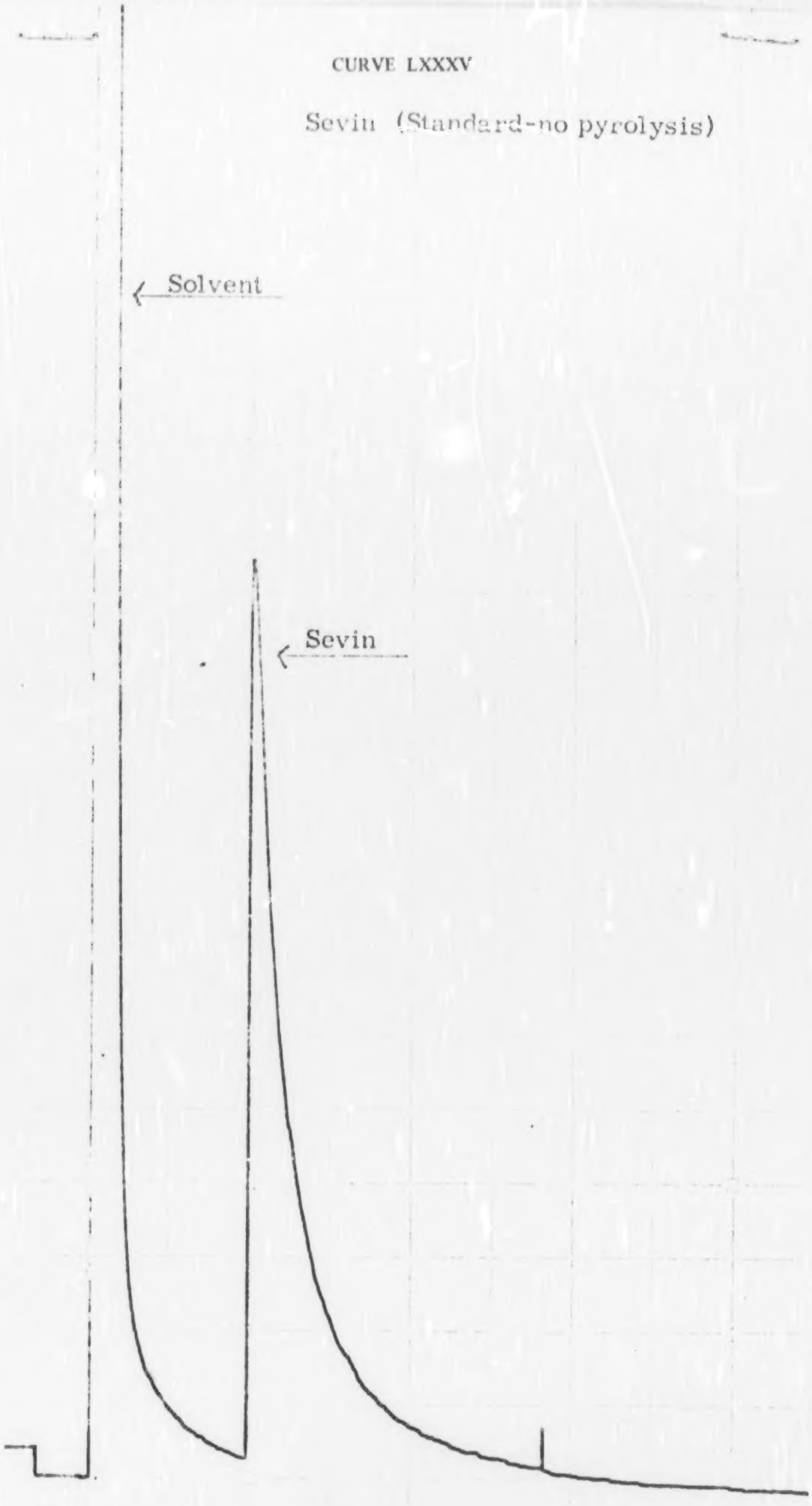
DSC of 0.6 Mg DDT
& 0.7 Mg $K_2Cr_2O_7$


CURVE LXXXIII
DSC of 0.9 Mg $K_2Cr_2O_7$
1.3 Mg Mineral Oil
Start 65°
endotherm
exotherm
211-356-A
No Condensation observed
End 500°
Charring


CURVE LXXXIV
DSC of 1.8 Mg DDT
1.3 Mg Mineral Oil
2.7 Mg $K_2Cr_2O_7$
Start 65°
endotherm
exotherm
211-356°C
112
117
Charring
End 500°

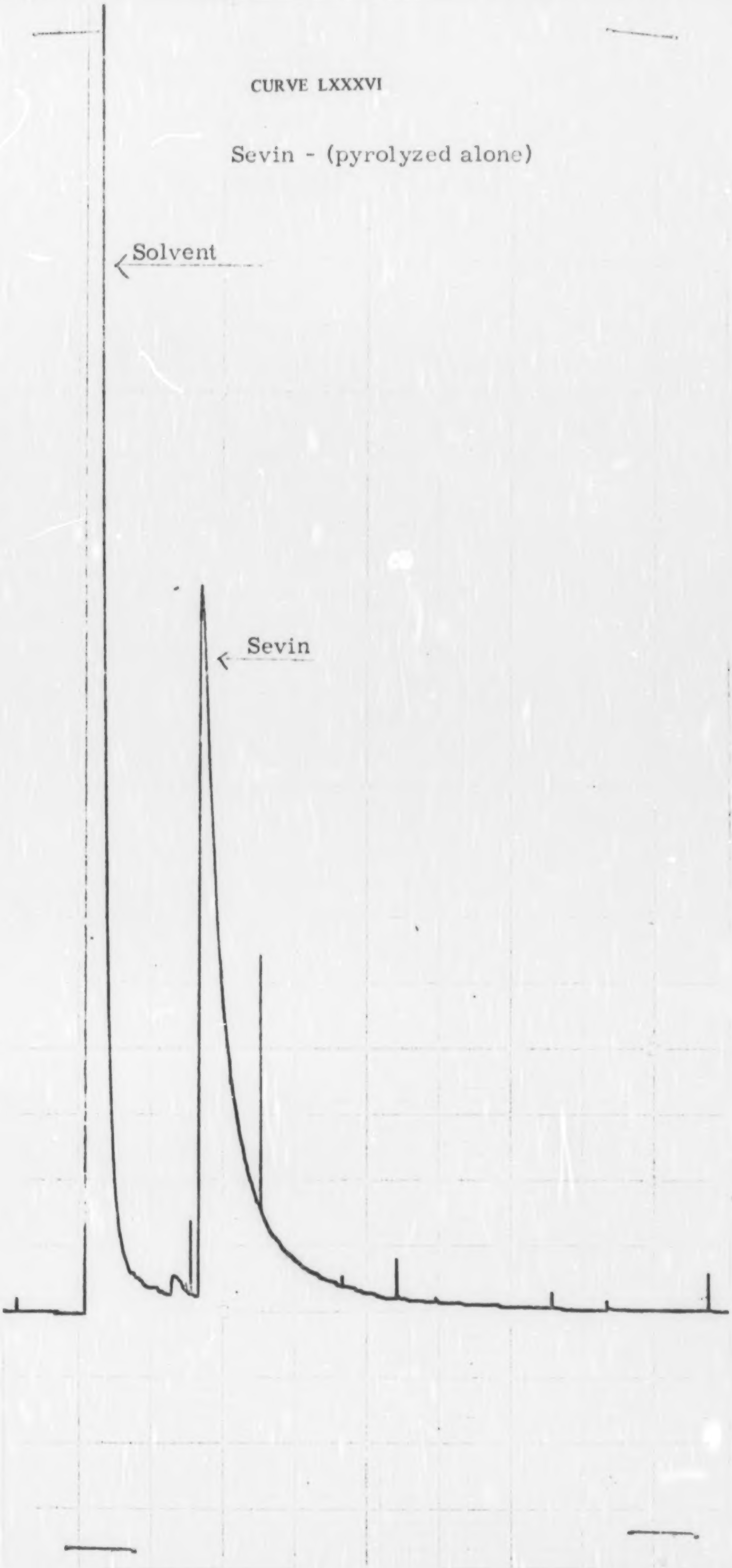
CURVE LXXXV

Sevin (Standard-no pyrolysis)



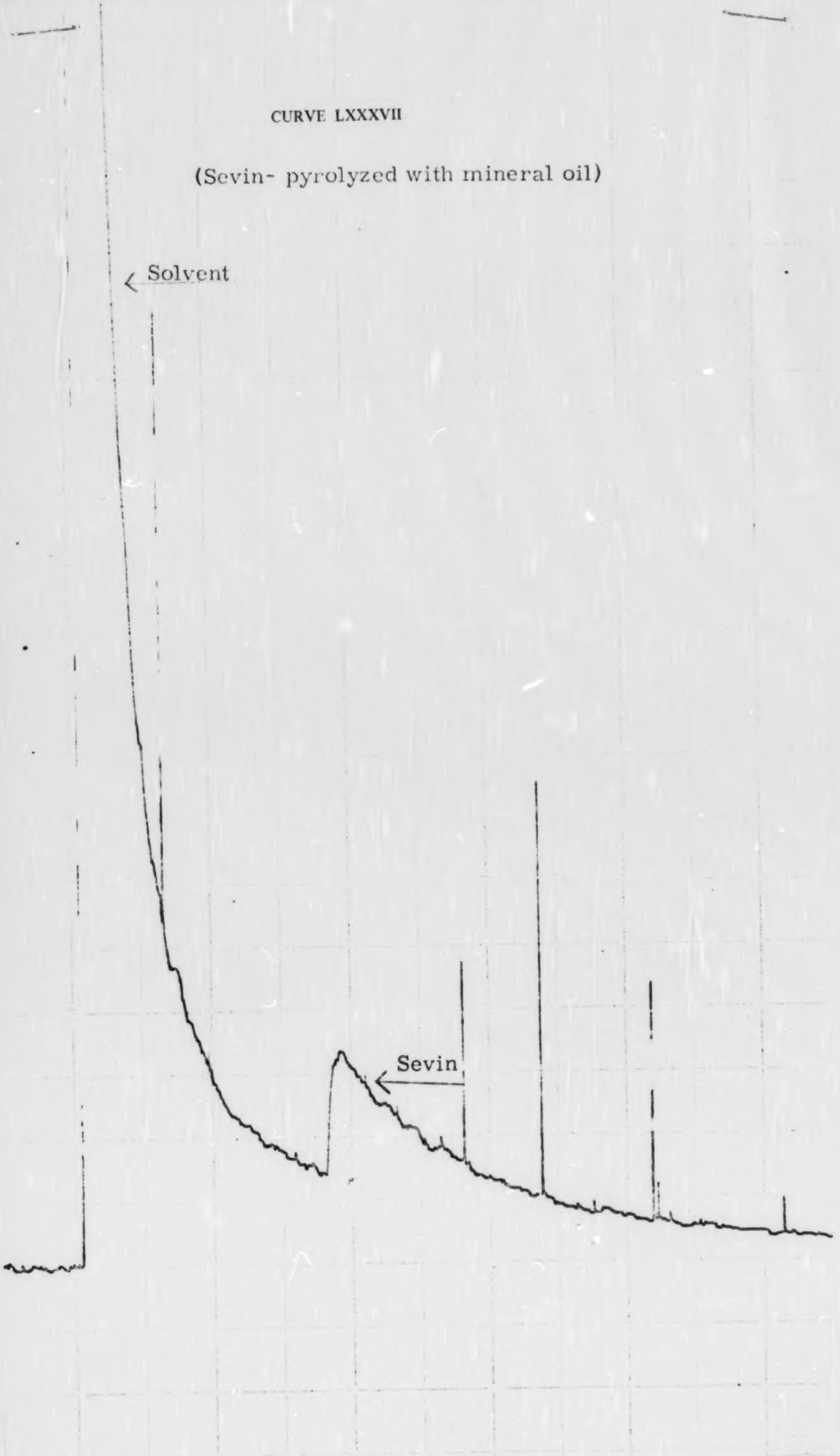
CURVE LXXXVI

Sevin - (pyrolyzed alone)



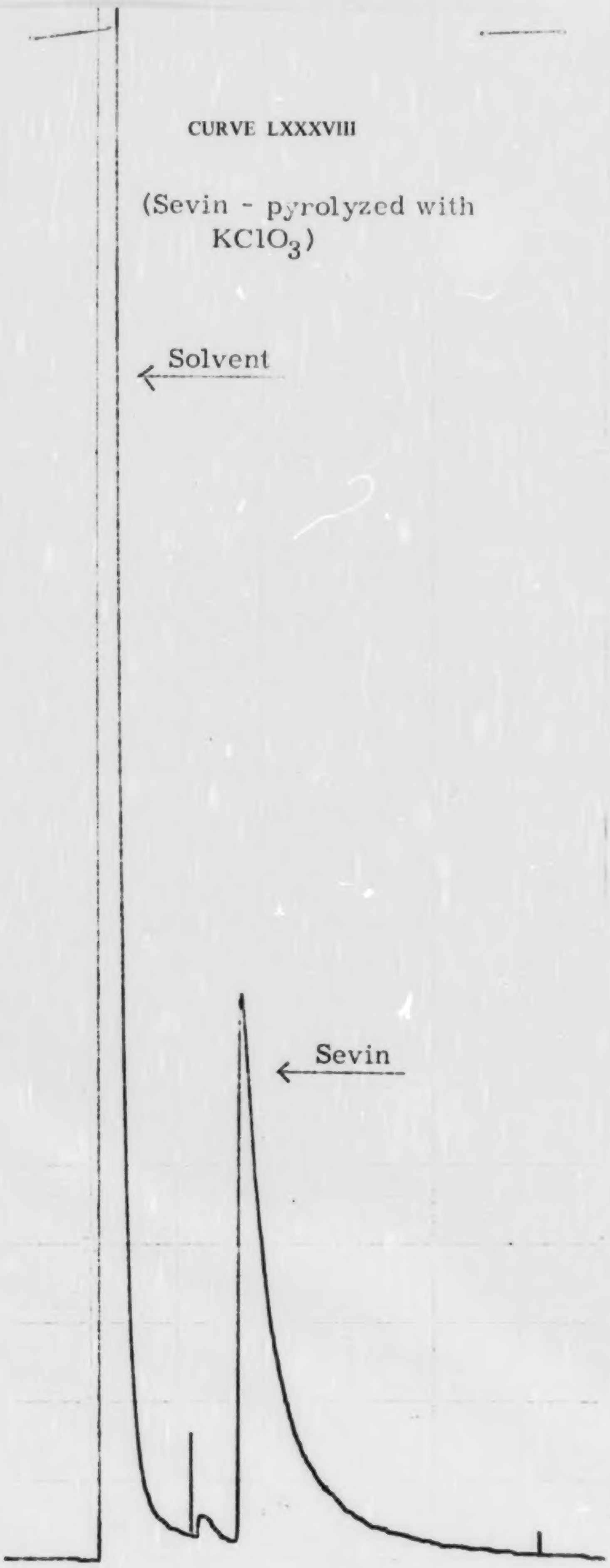
CURVE LXXXVII

(Sevin- pyrolyzed with mineral oil)



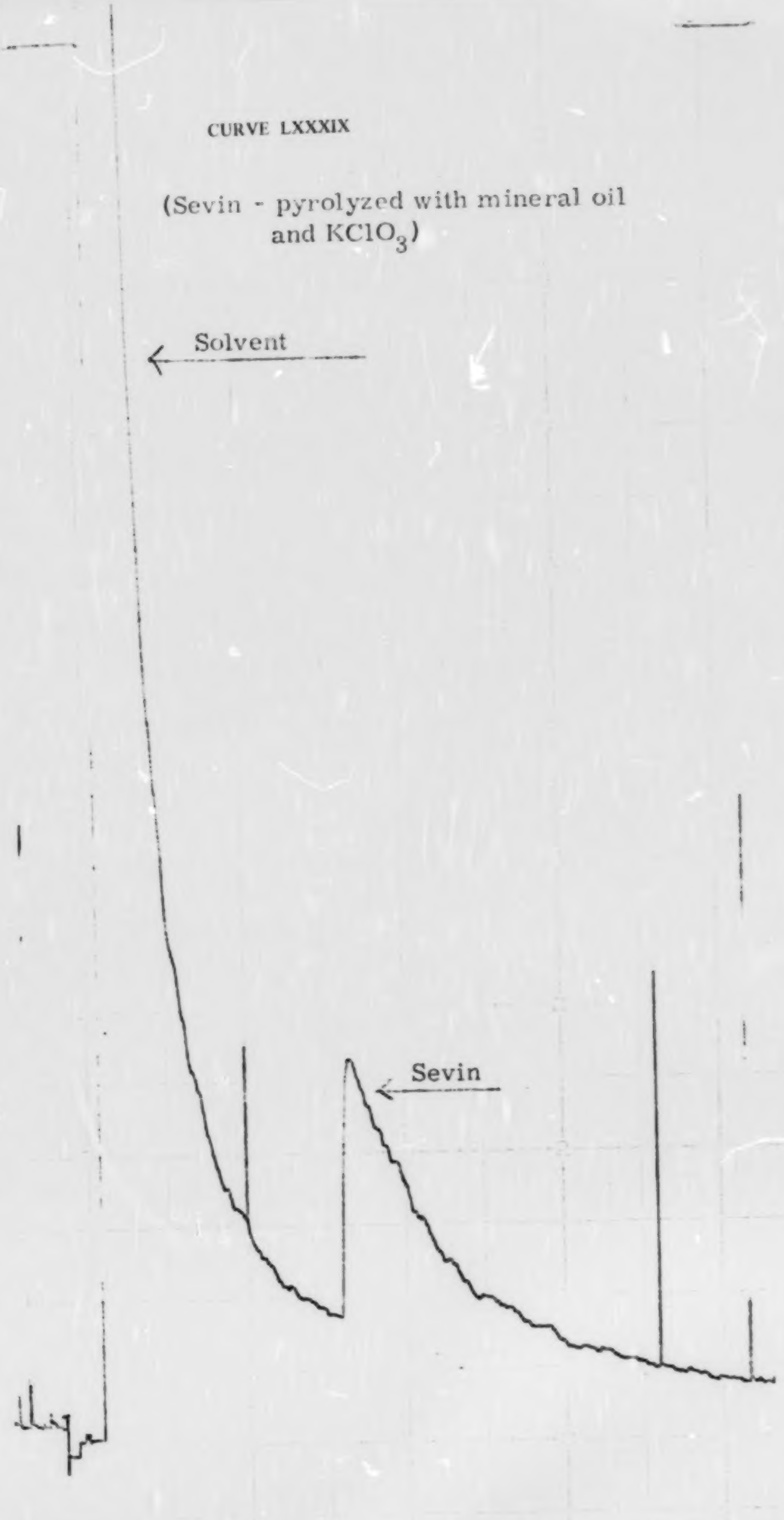
CURVE LXXXVIII

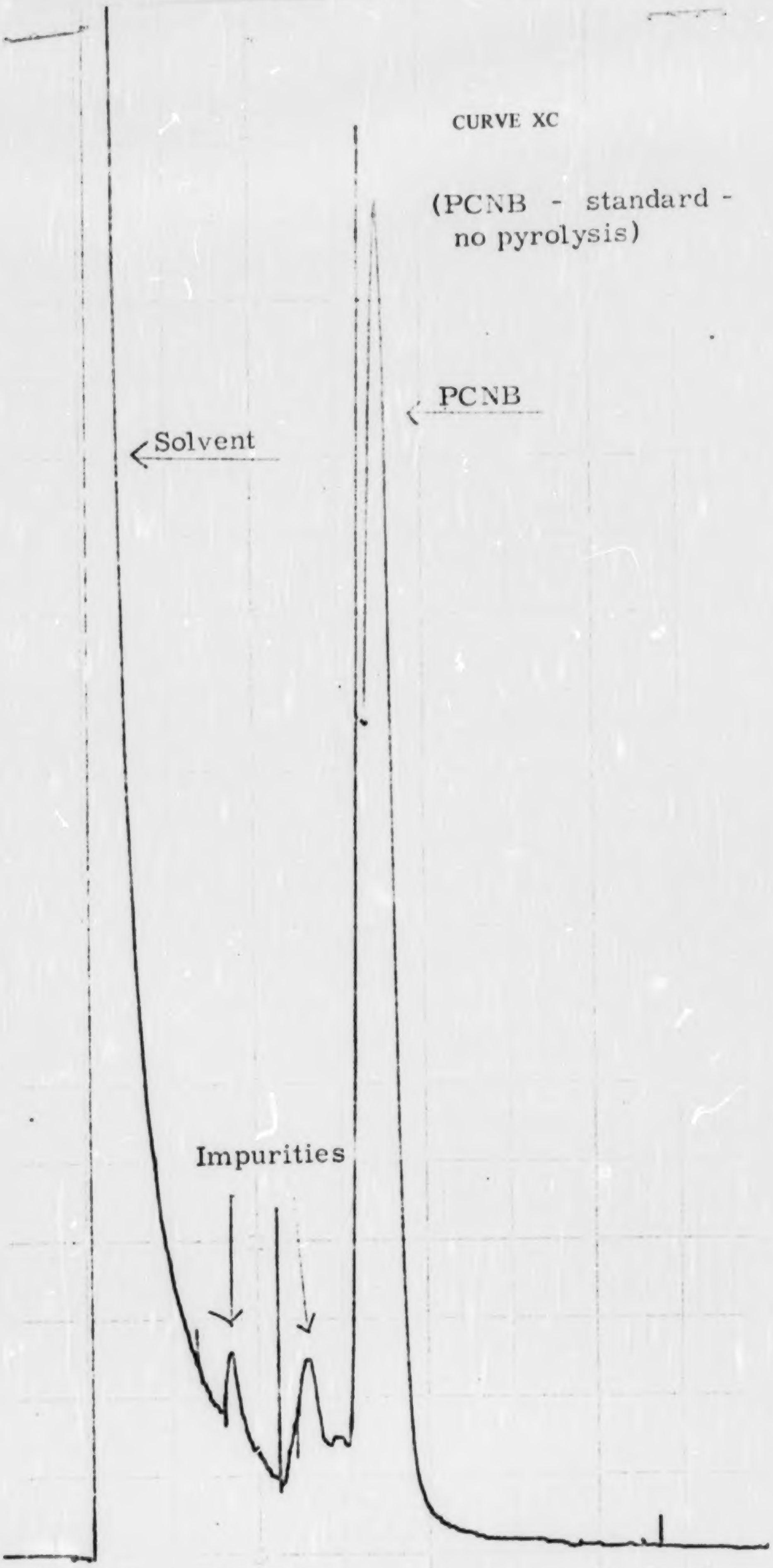
(Sevin - pyrolyzed with $KClO_3$)



CURVE LXXXIX

(Sevin - pyrolyzed with mineral oil and $KClO_3$)

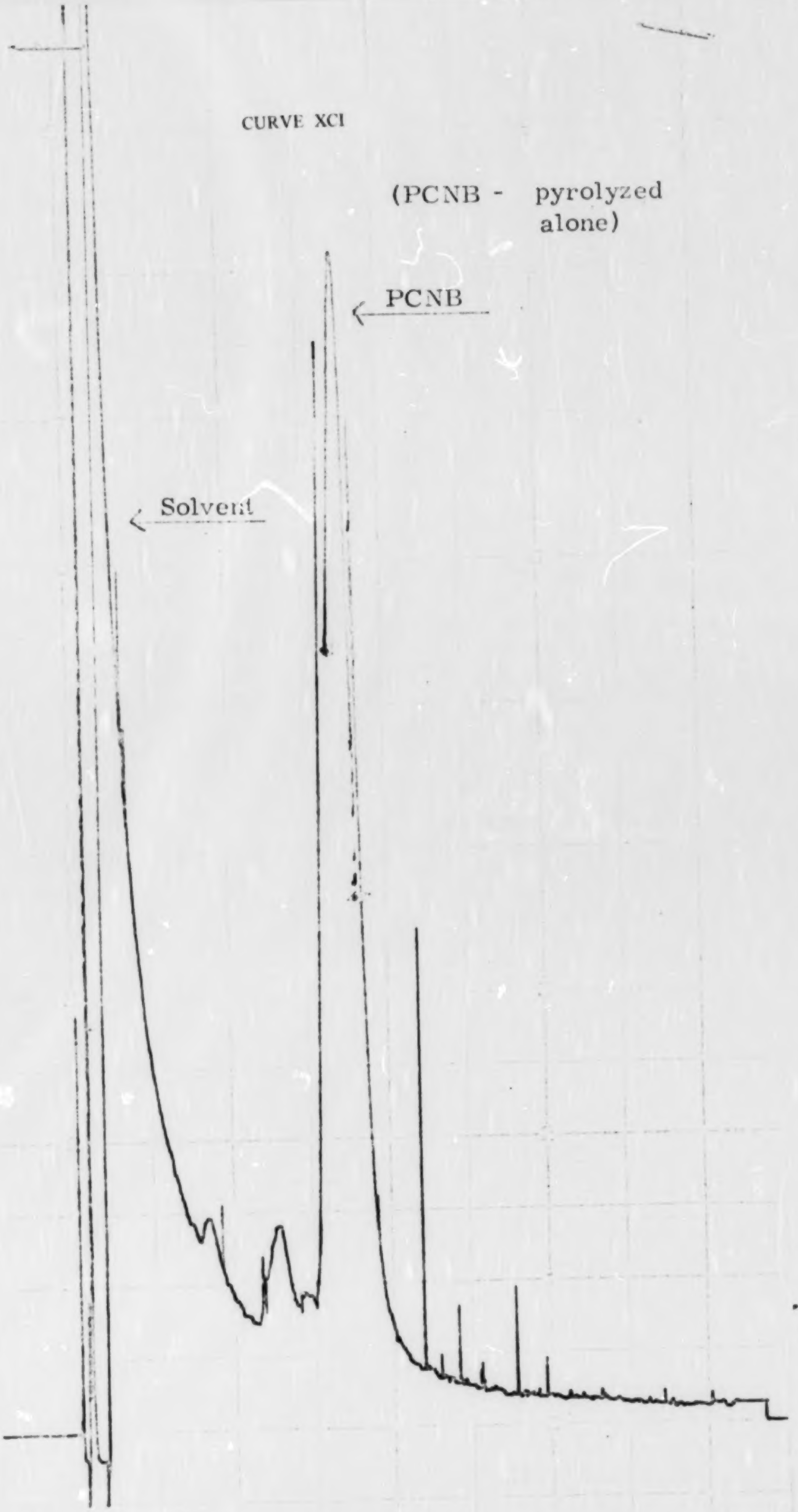


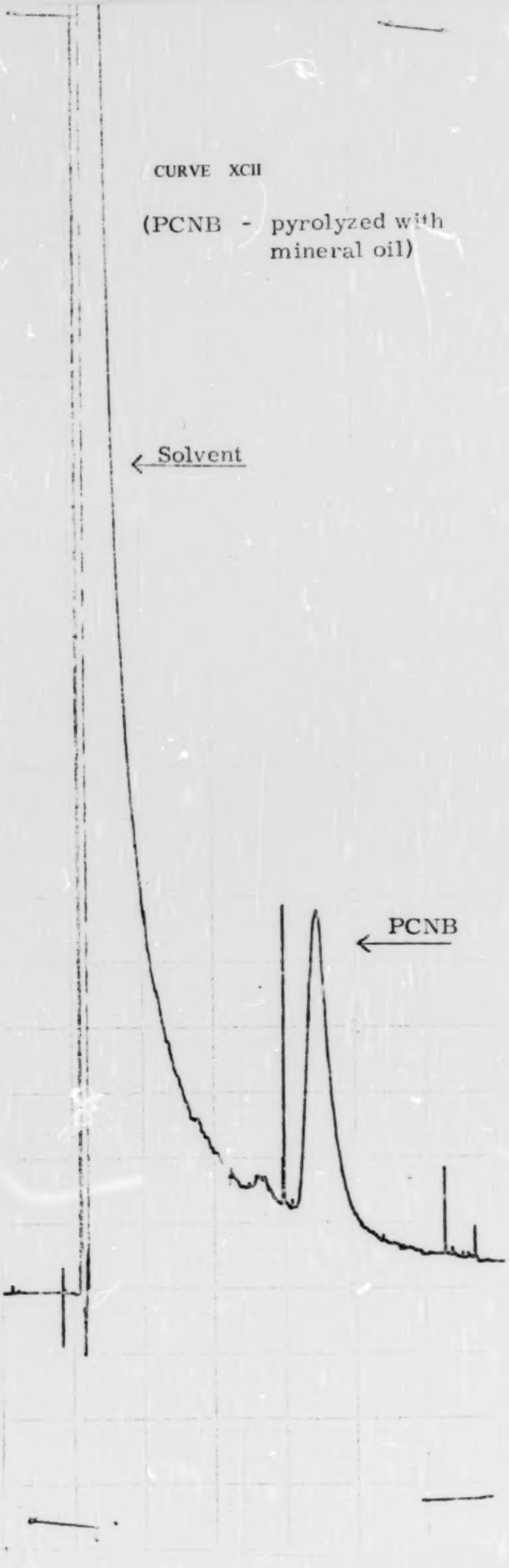


CURVE XC

(PCNB - standard - no pyrolysis)

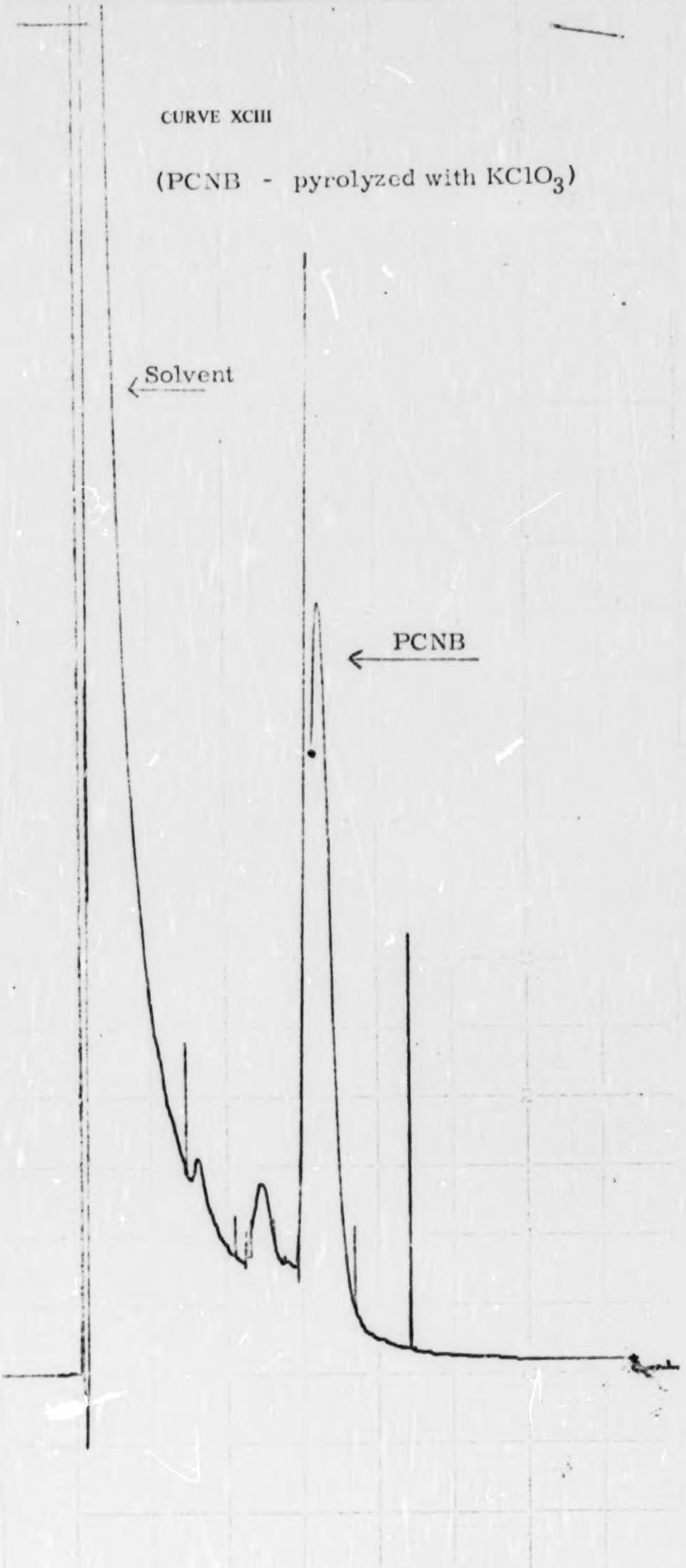
CURVE XCI




CURVE XCII
(PCNB - pyrolyzed with mineral oil)
Solvent
PCNB

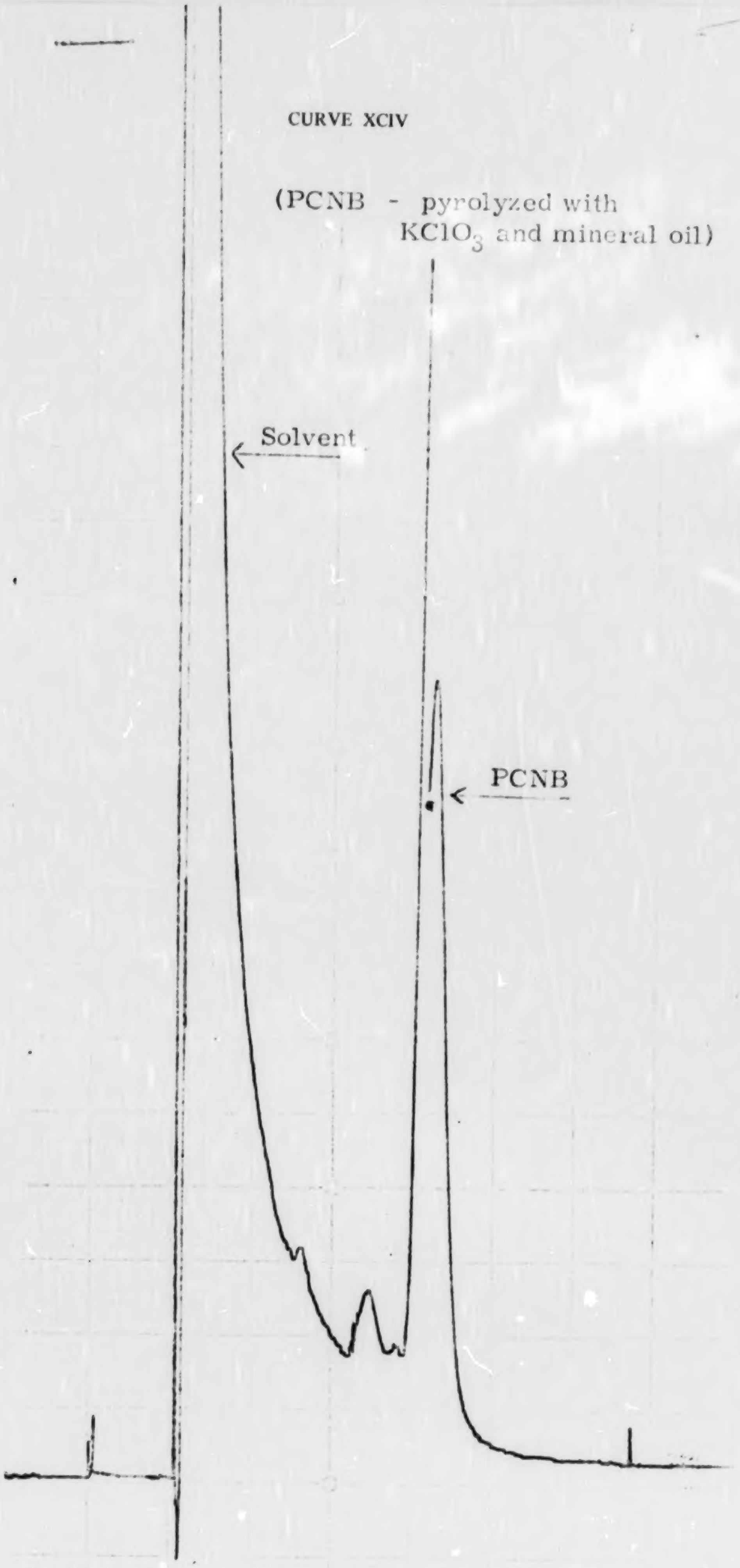
CURVE XCIII

(PCNB - pyrolyzed with $KClO_3$)



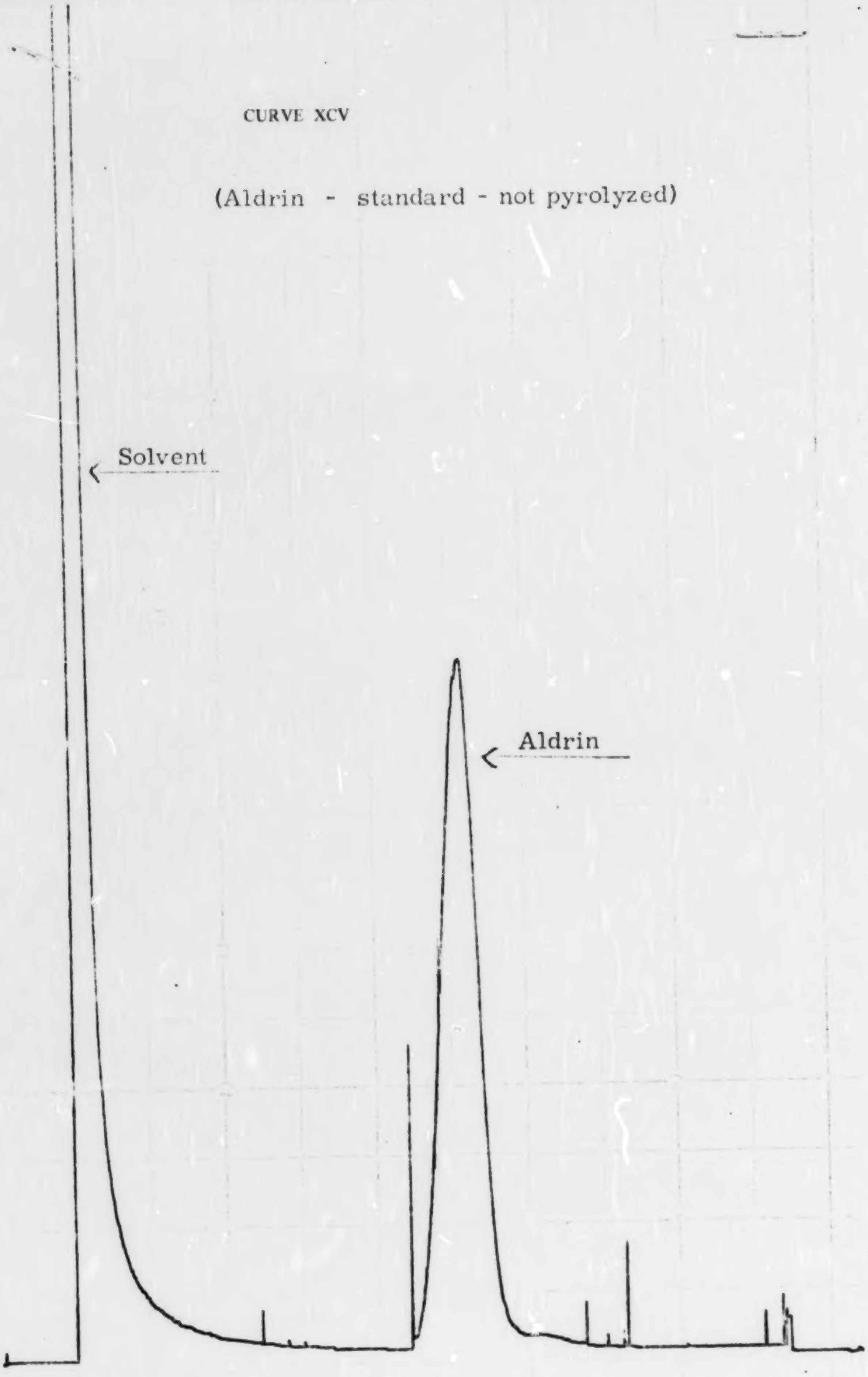
CURVE XCIV

(PCNB - pyrolyzed with $KClO_3$ and mineral oil)



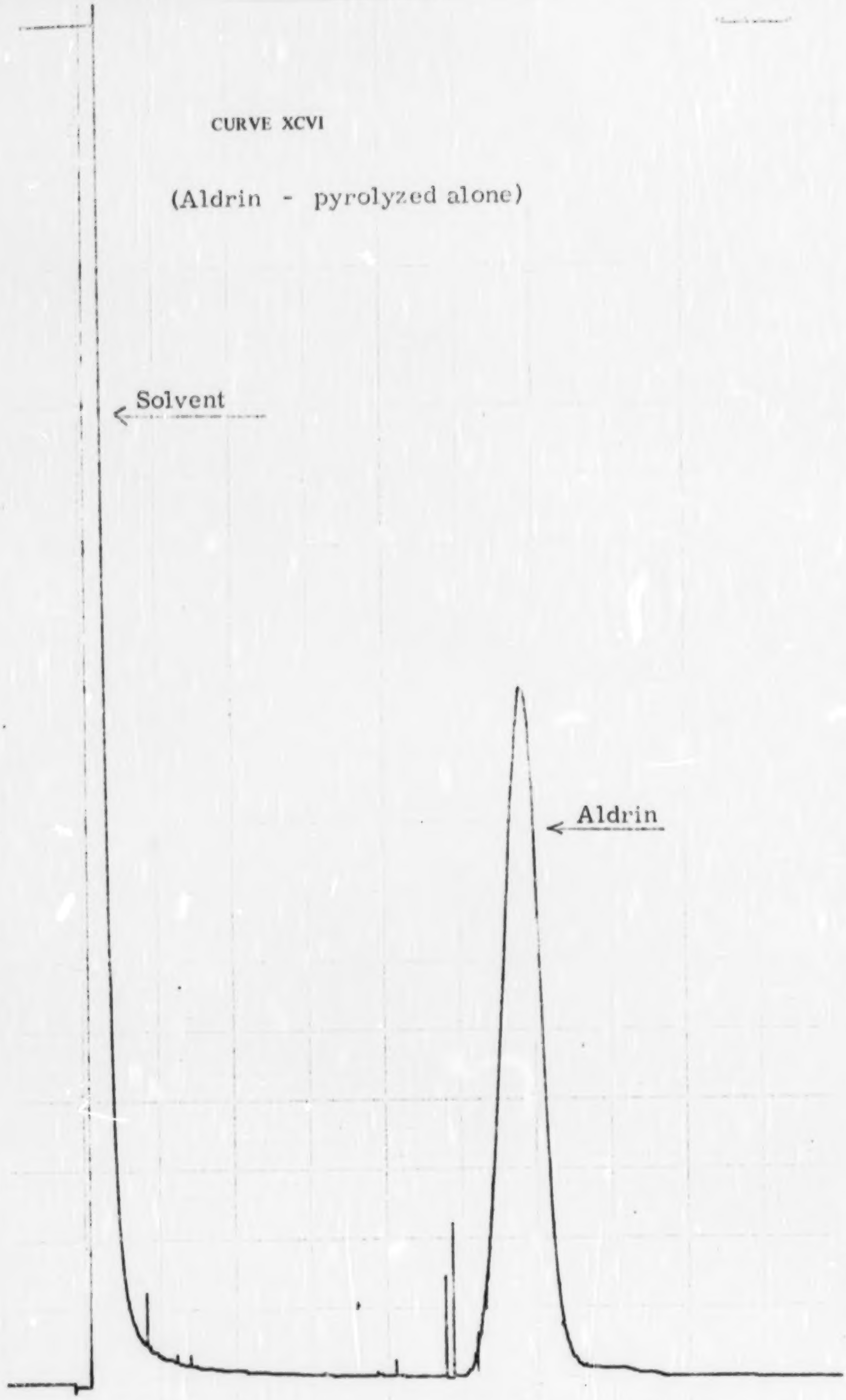
CURVE XCV

(Aldrin - standard - not pyrolyzed)

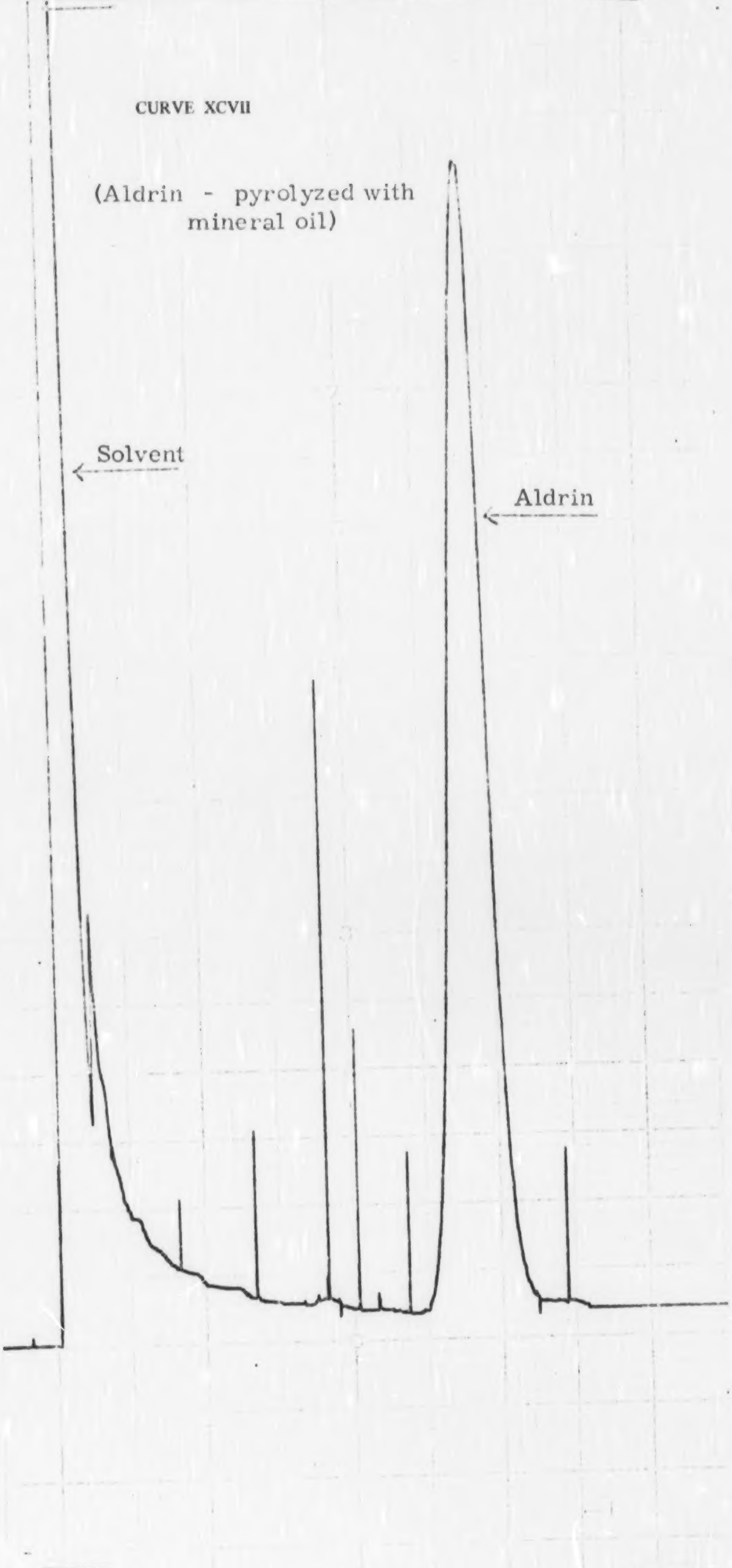


CURVE XCVI

(Aldrin - pyrolyzed alone)



5μl

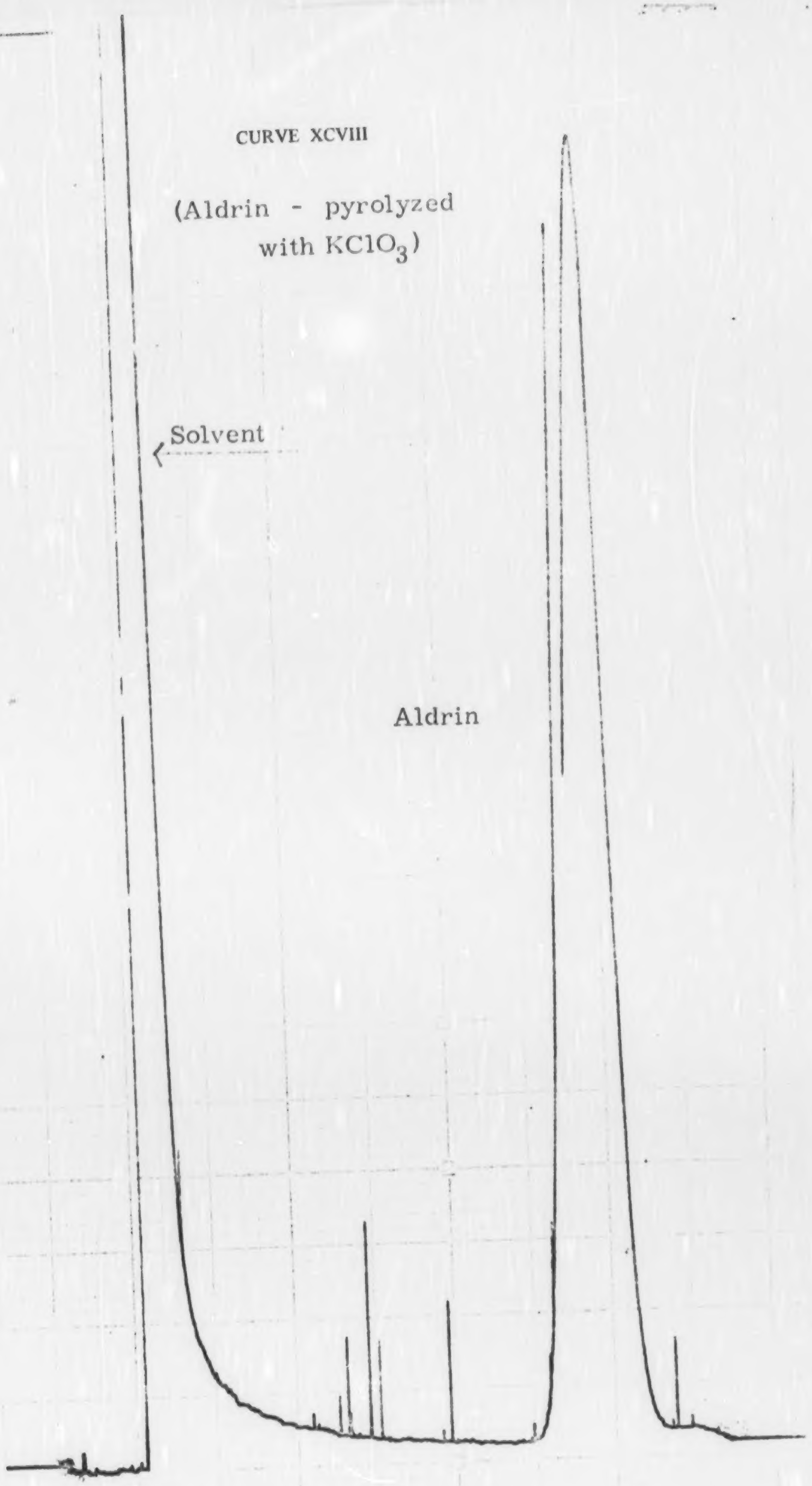


CURVE XCVII

(Aldrin - pyrolyzed with mineral oil)

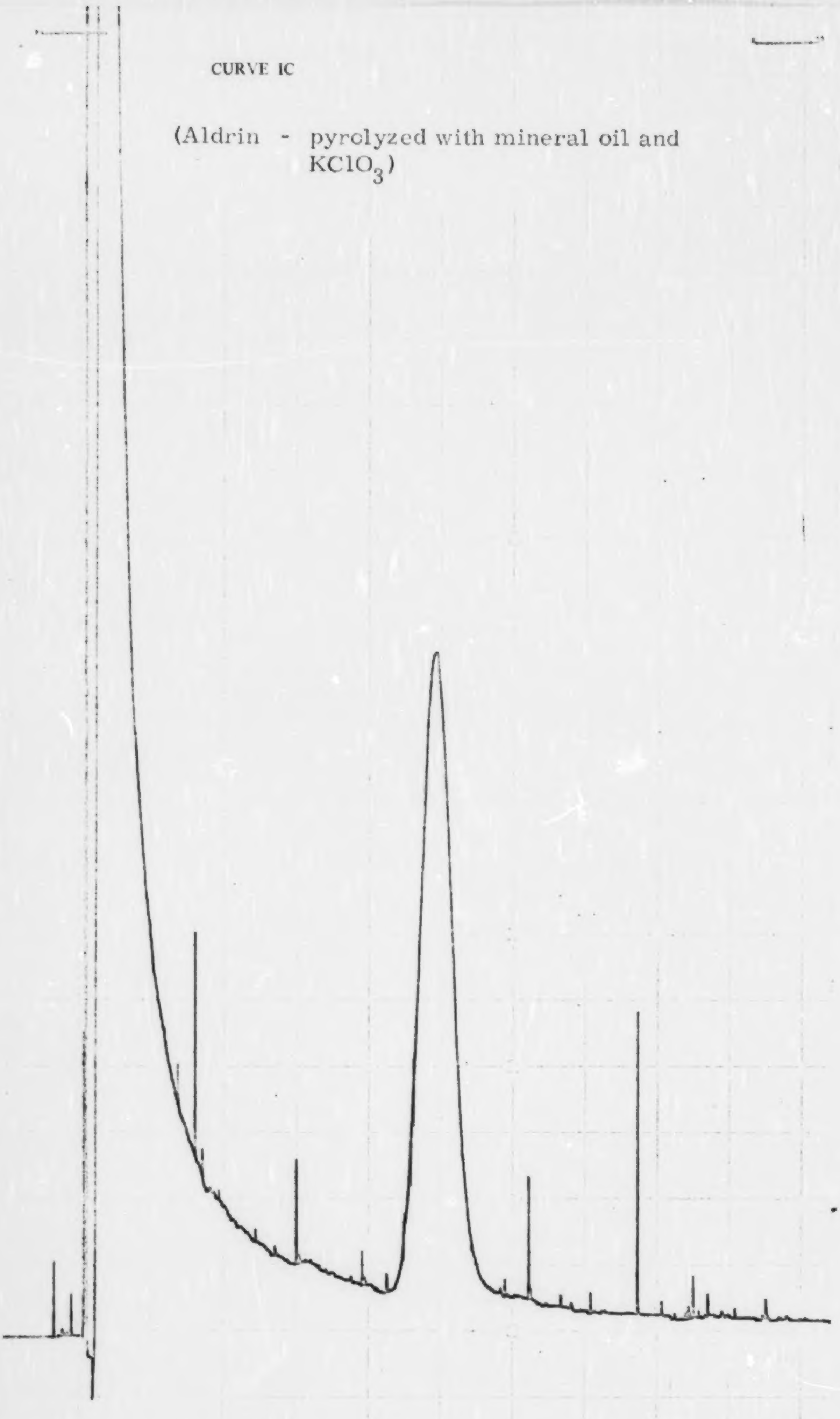
CURVE XCVIII

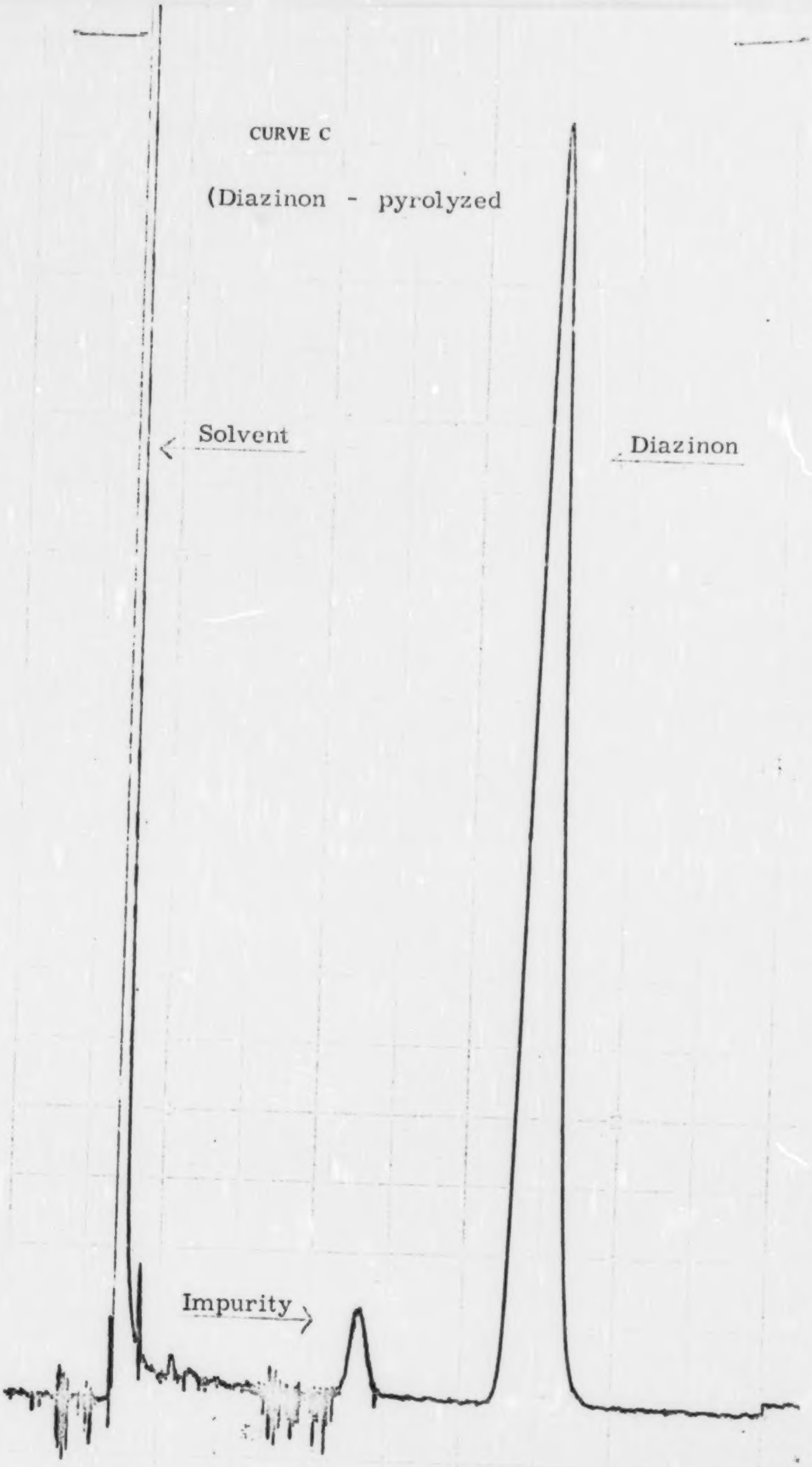
(Aldrin - pyrolyzed with $KClO_3$)



CURVE IC

(Aldrin - pyrolyzed with mineral oil and $KClO_3$)



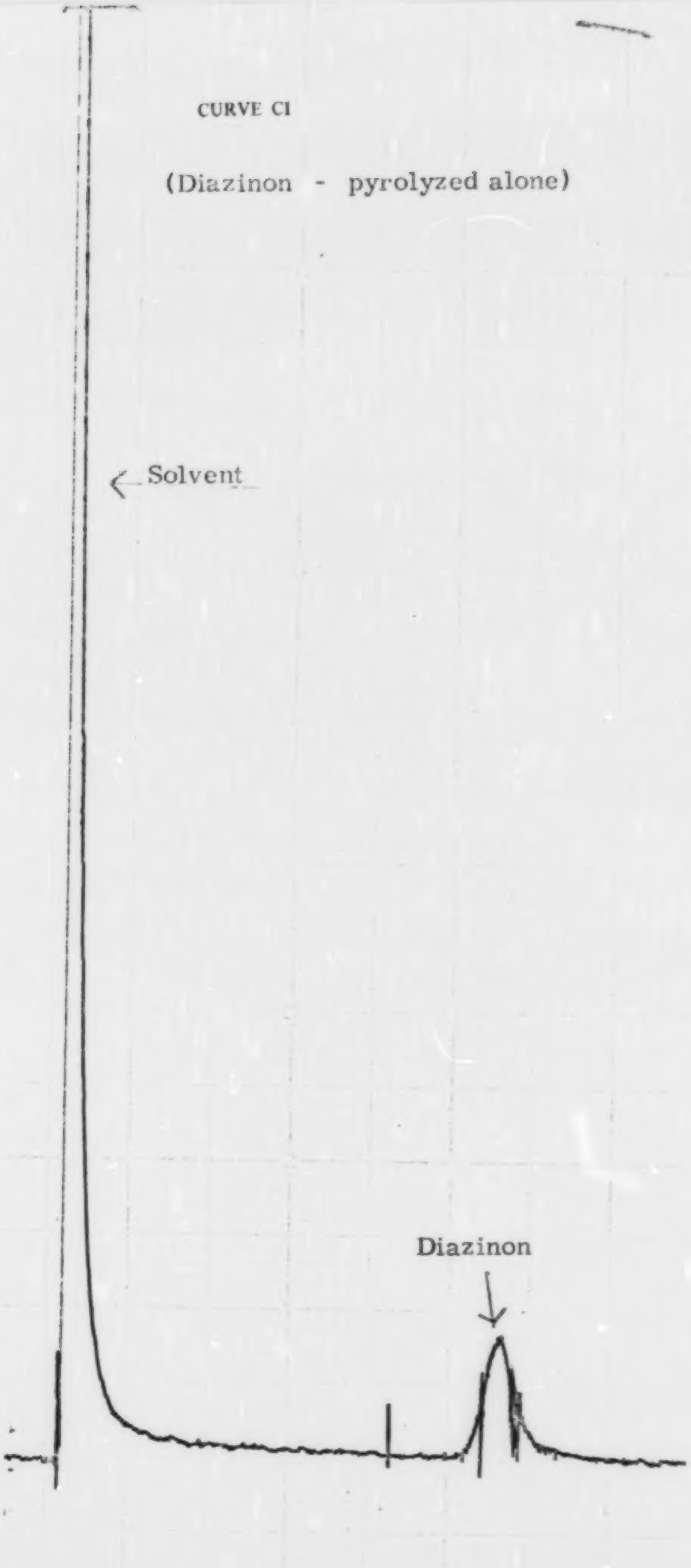


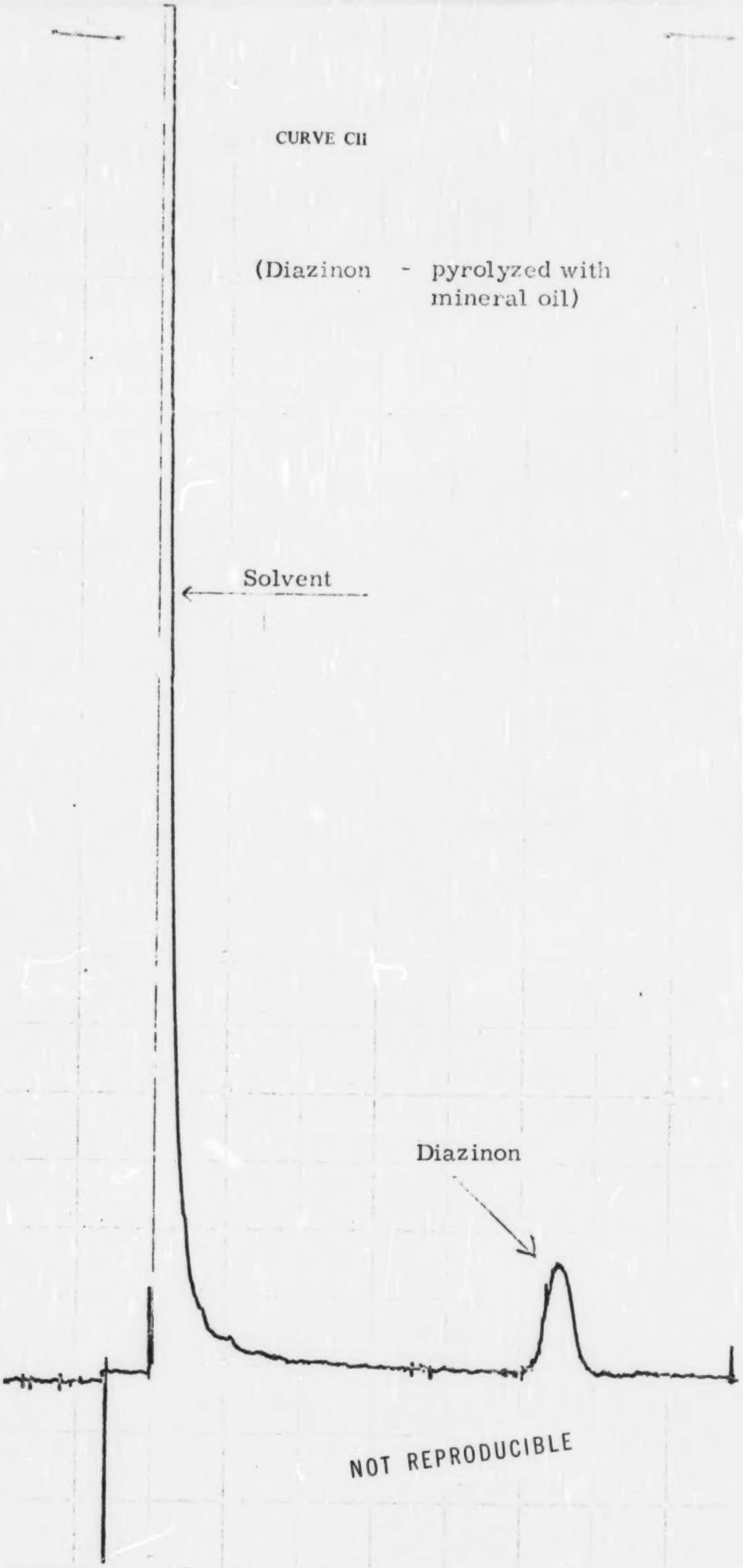
CURVE C

(Diazinon - pyrolyzed

CURVE CI

(Diazinon - pyrolyzed alone)





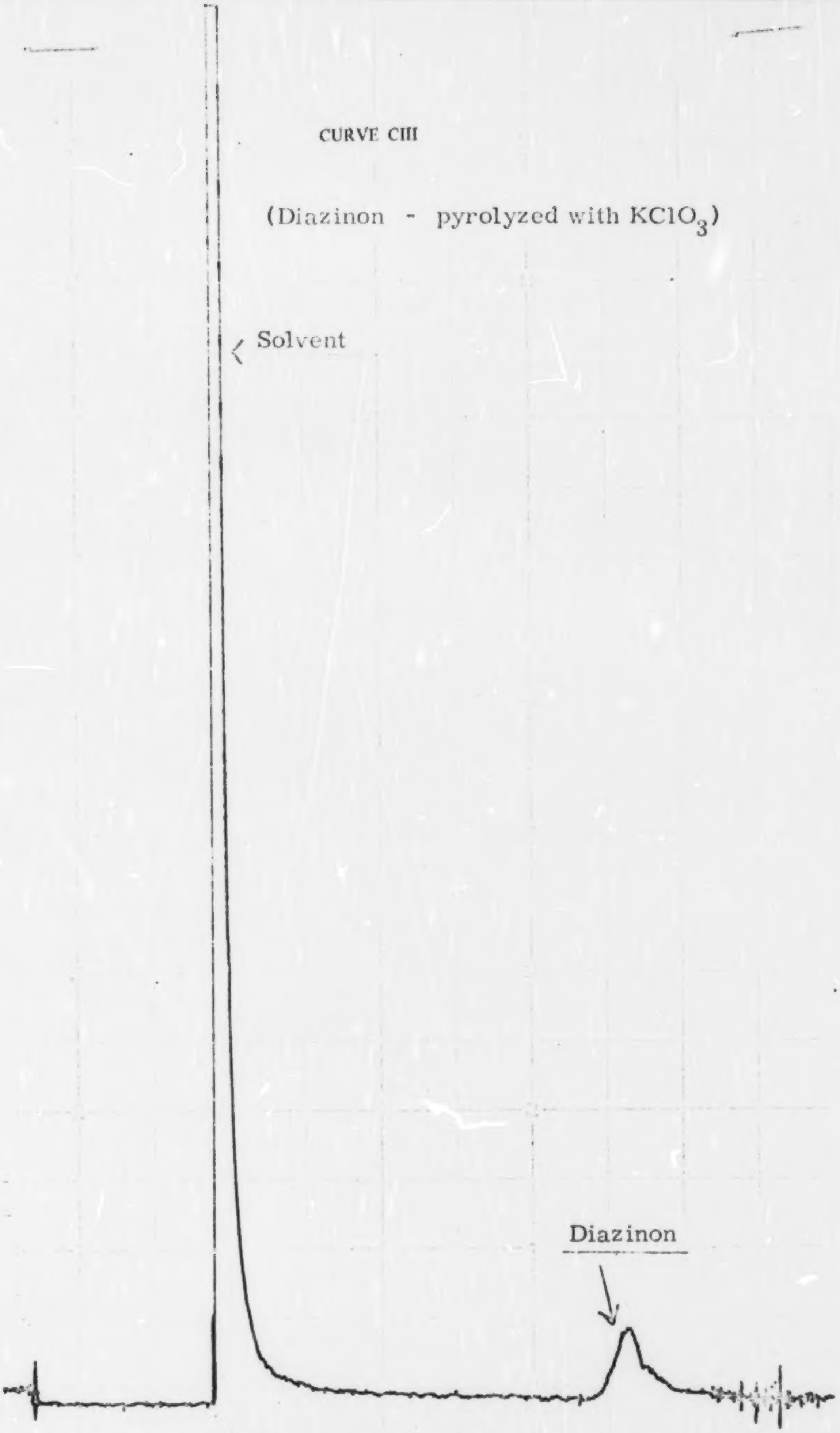
CURVE CII

(Diazinon - pyrolyzed with mineral oil)

NOT REPRODUCIBLE

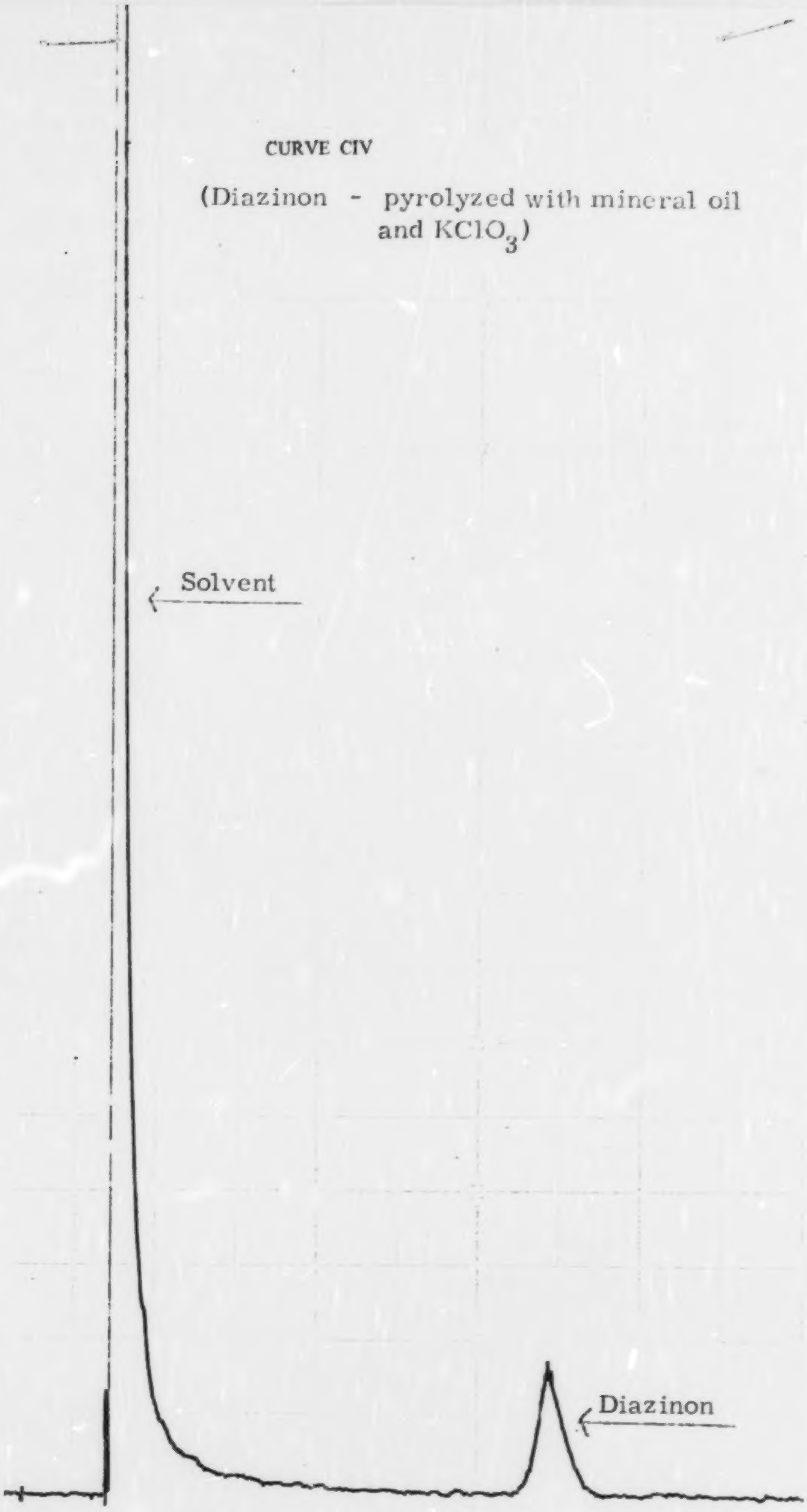
CURVE CIII

(Diazinon - pyrolyzed with $KClO_3$)



CURVE CIV

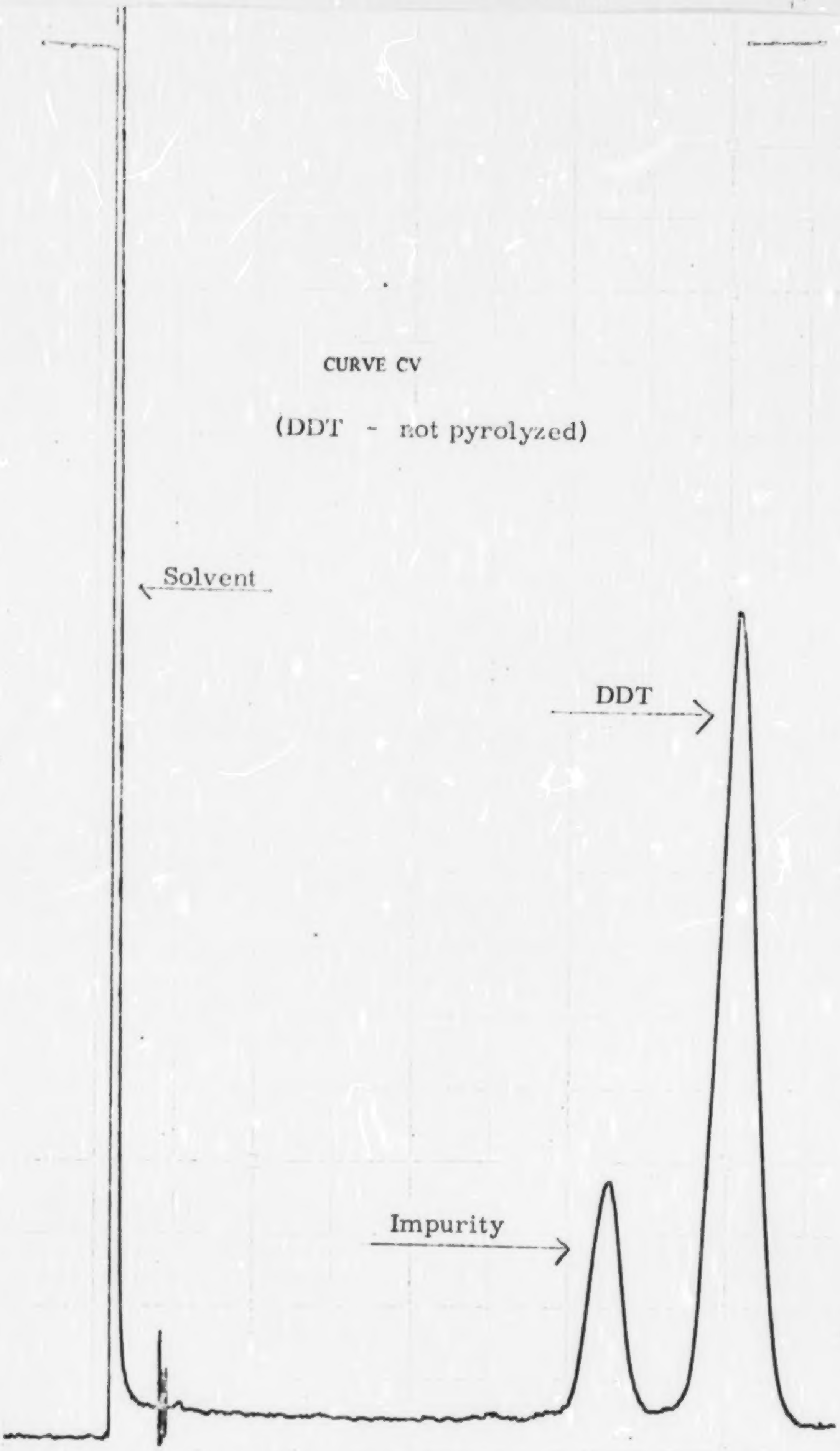
(Diazinon - pyrolyzed with mineral oil and $KClO_3$)



NOT REPRODUCIBLE

CURVE CV

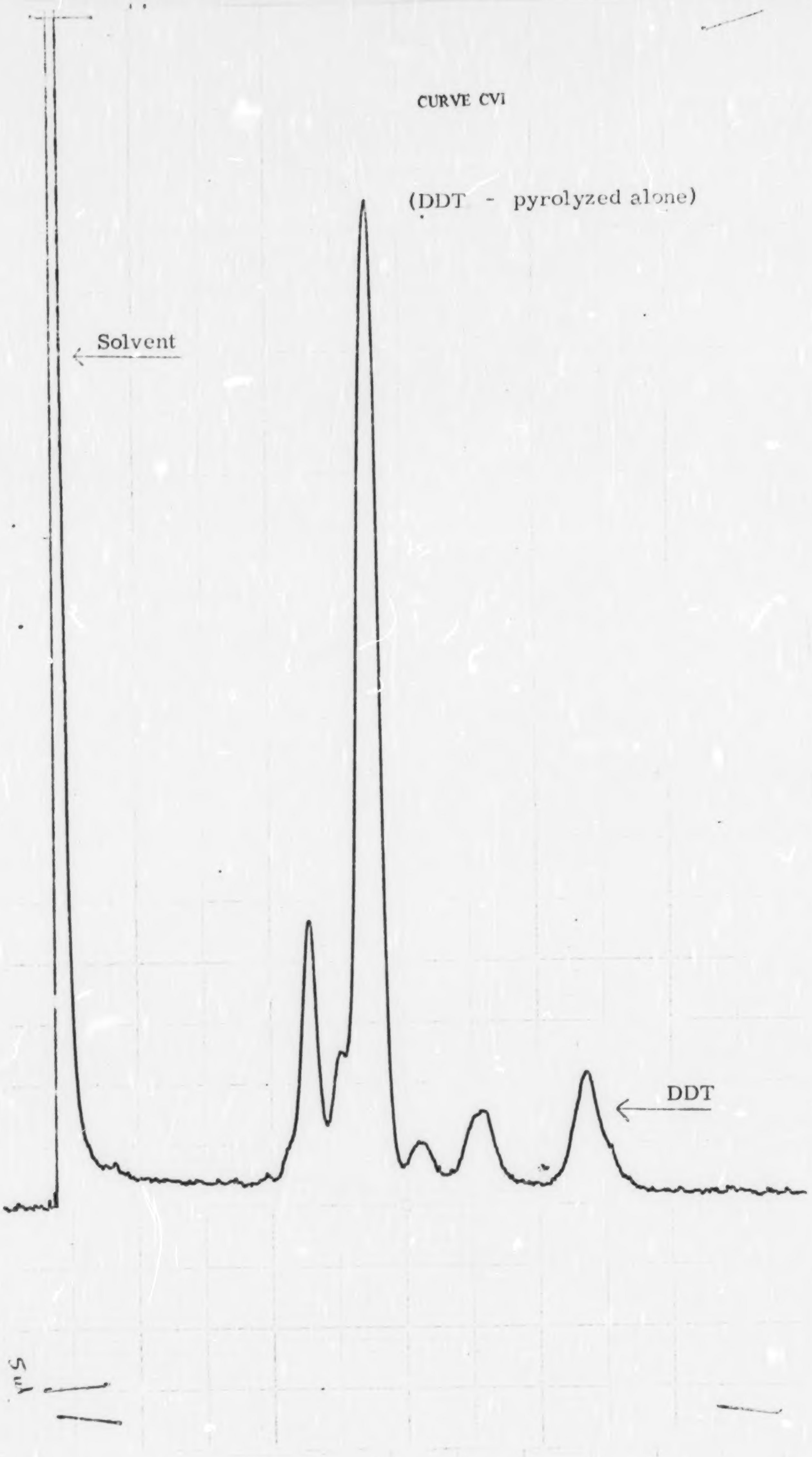
(DDT - not pyrolyzed)



NOT REPRODUCIBLE

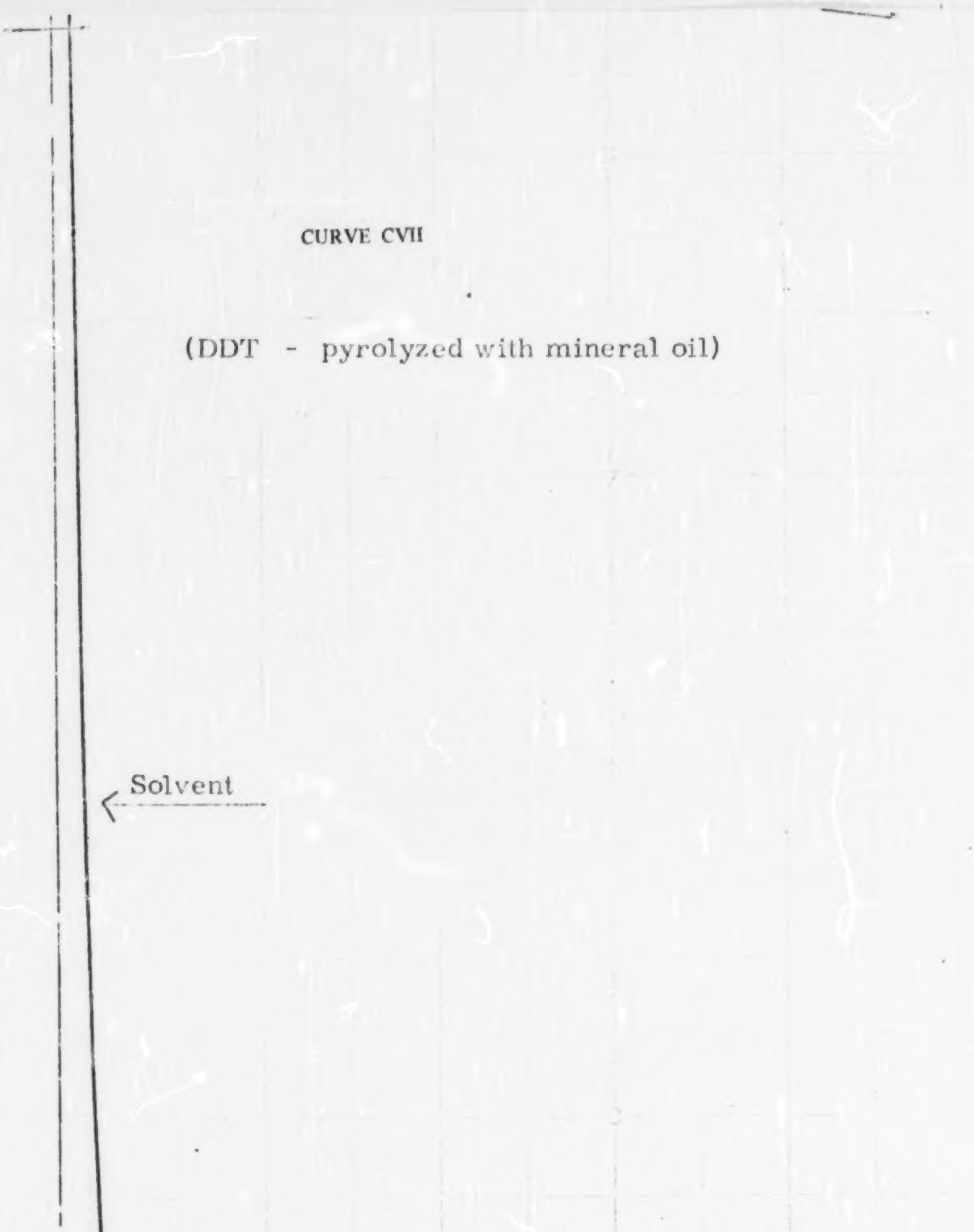
CURVE CVI

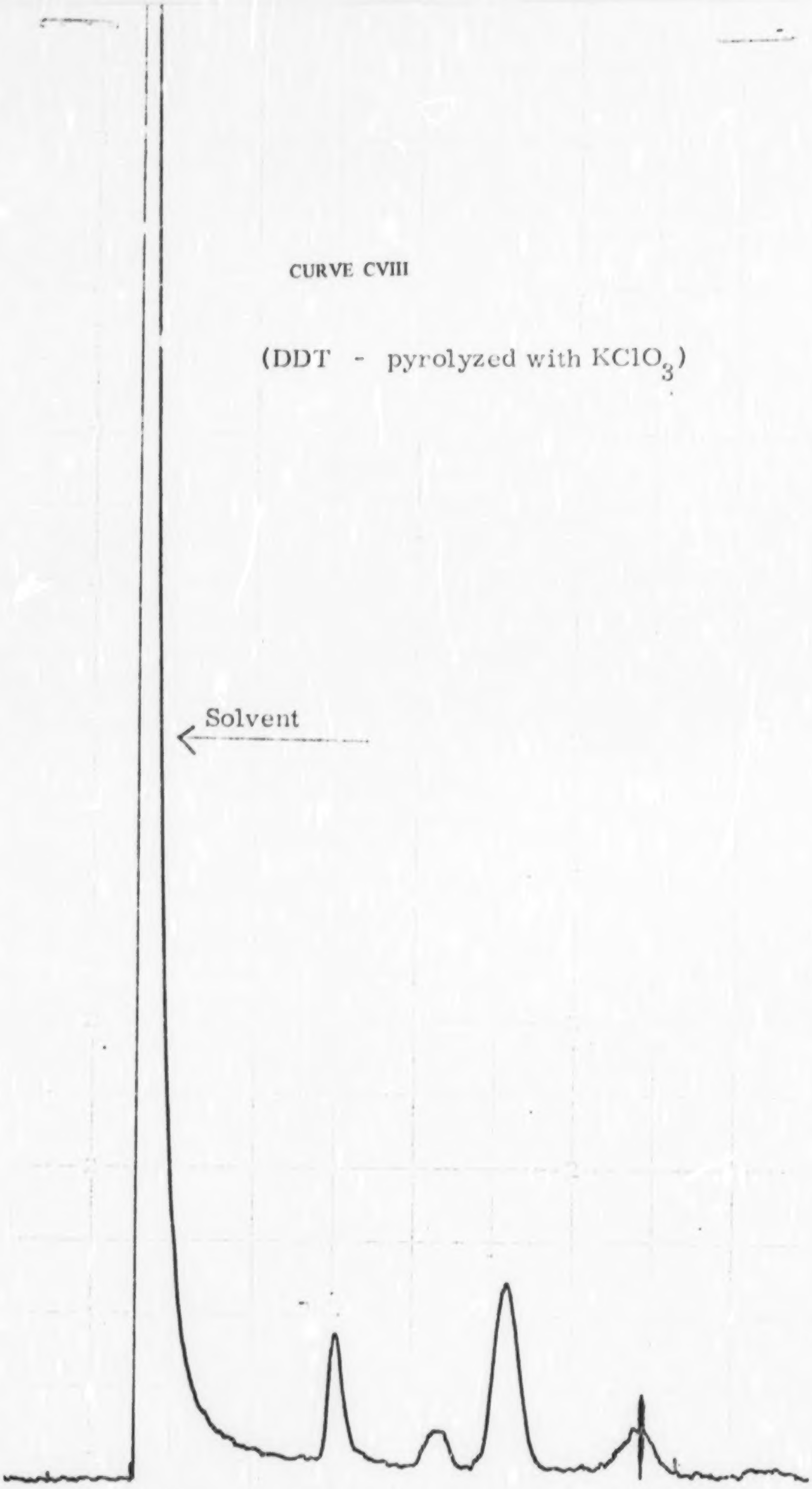
(DDT - pyrolyzed alone)



CURVE CVII

(DDT - pyrolyzed with mineral oil)



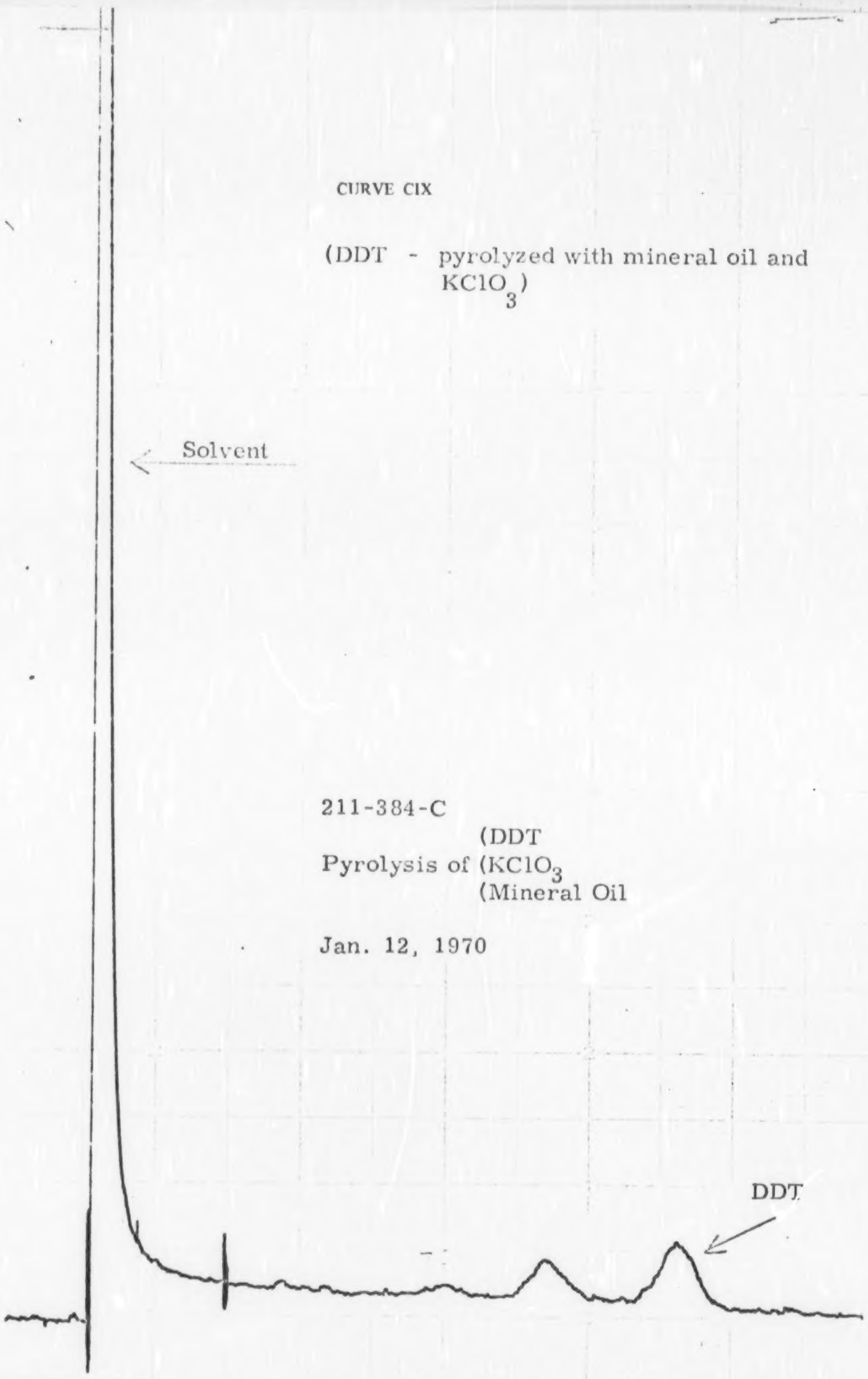


CURVE CVIII

(DDT - pyrolyzed with $KClO_3$)

CURVE CIX

(DDT - pyrolyzed with mineral oil and $KClO_3$)



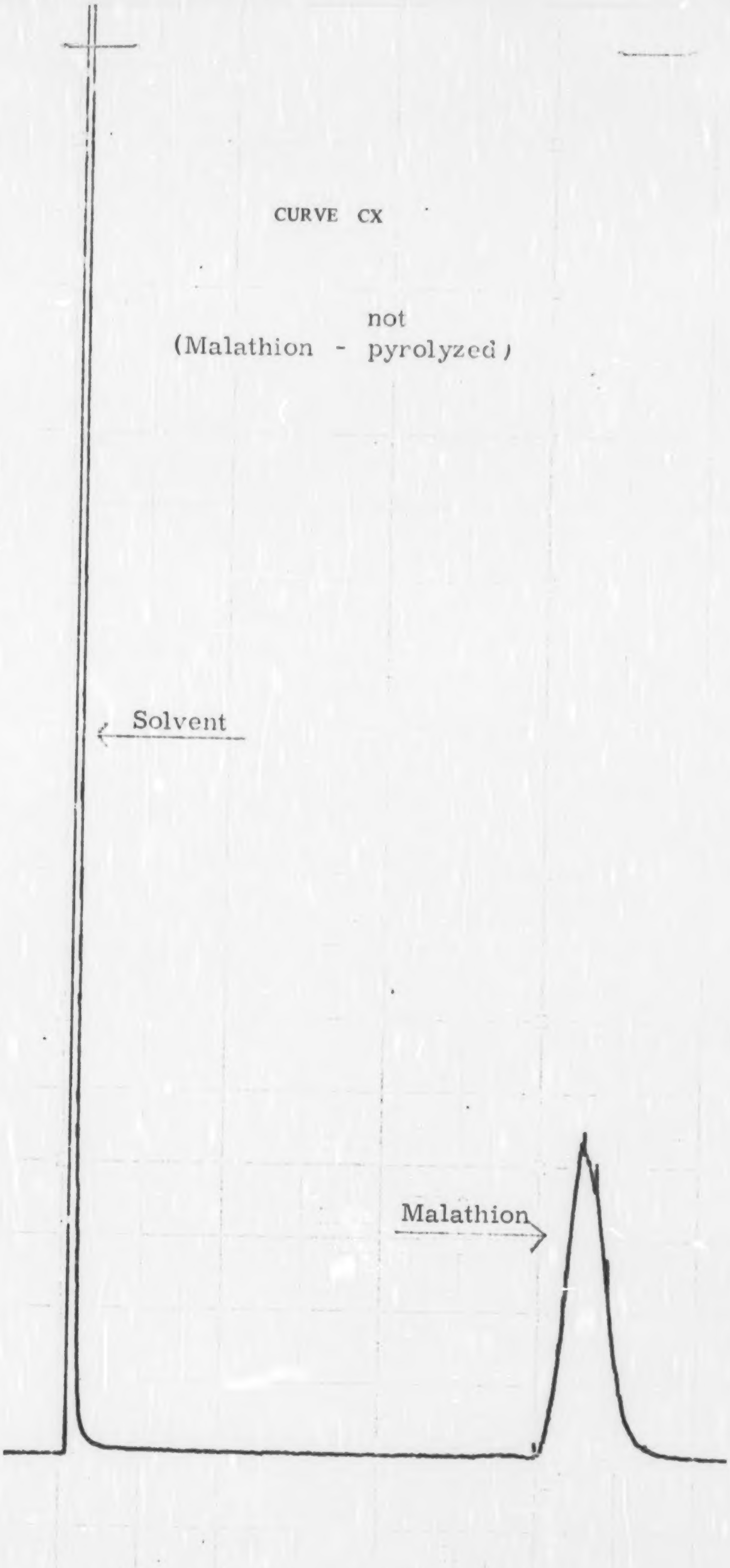
211-384-C

Pyrolysis of (DDT
(KClO$_3$
(Mineral Oil

Jan. 12, 1970

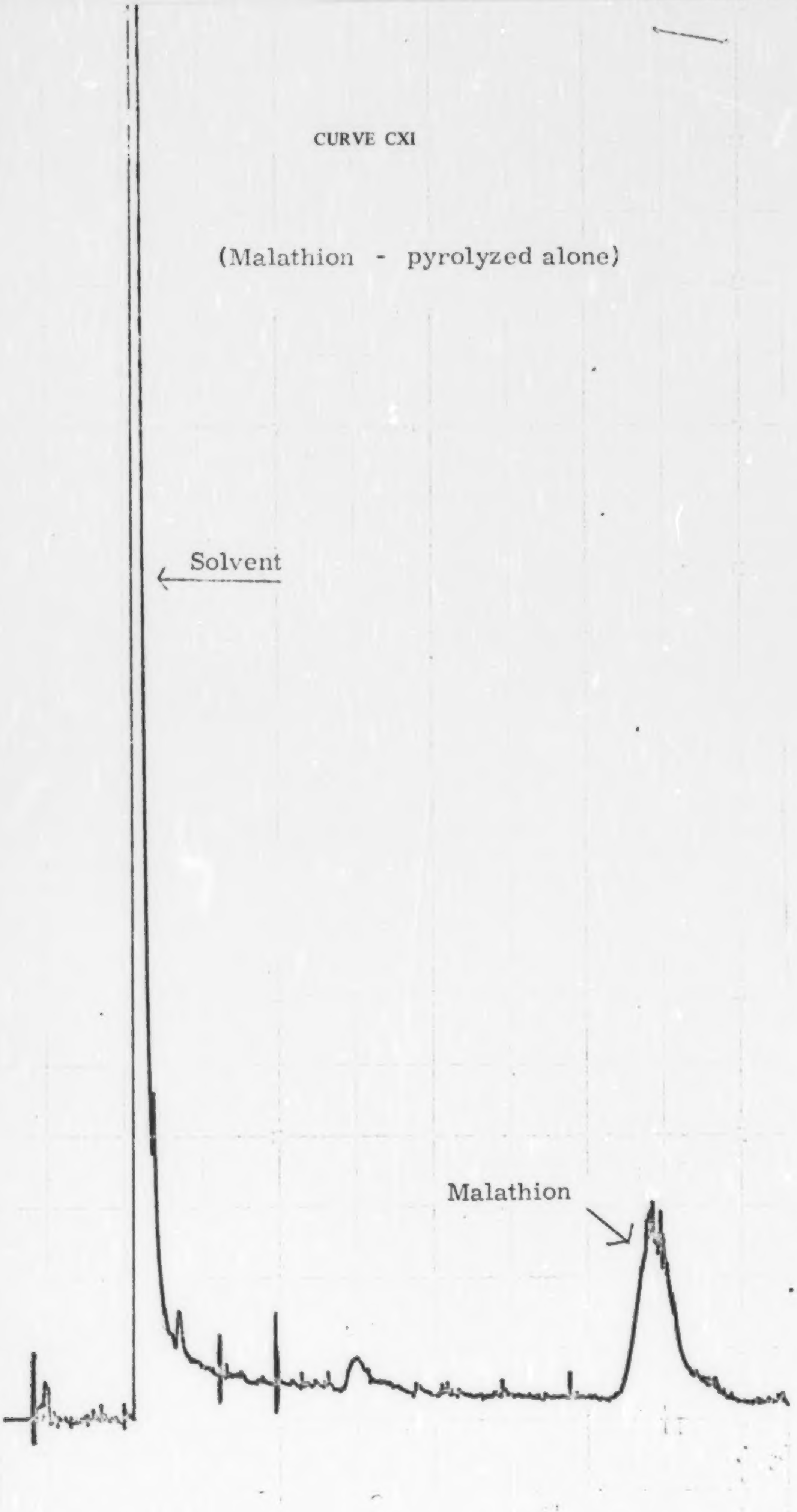
CURVE CX

(Malathion - not pyrolyzed)

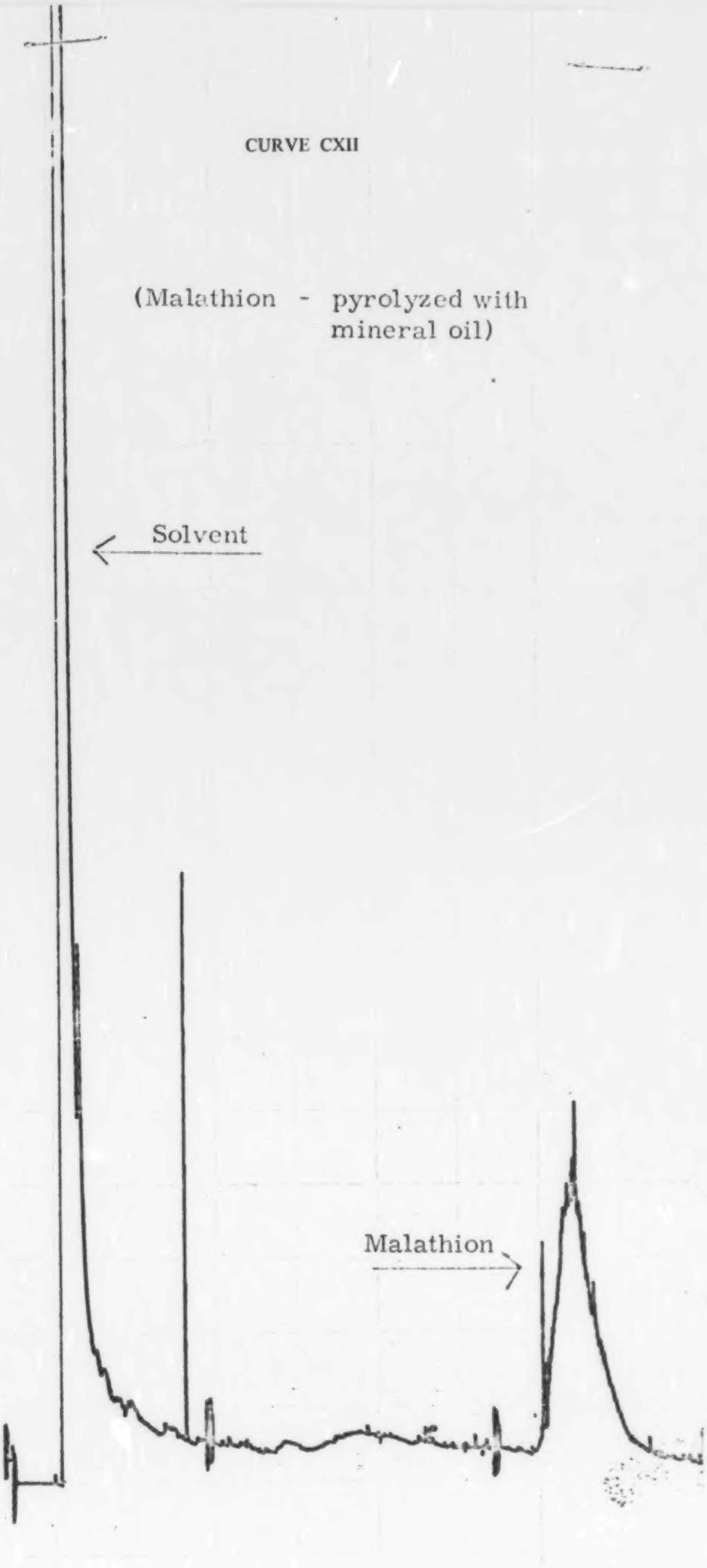


CURVE CXI

(Malathion - pyrolyzed alone)



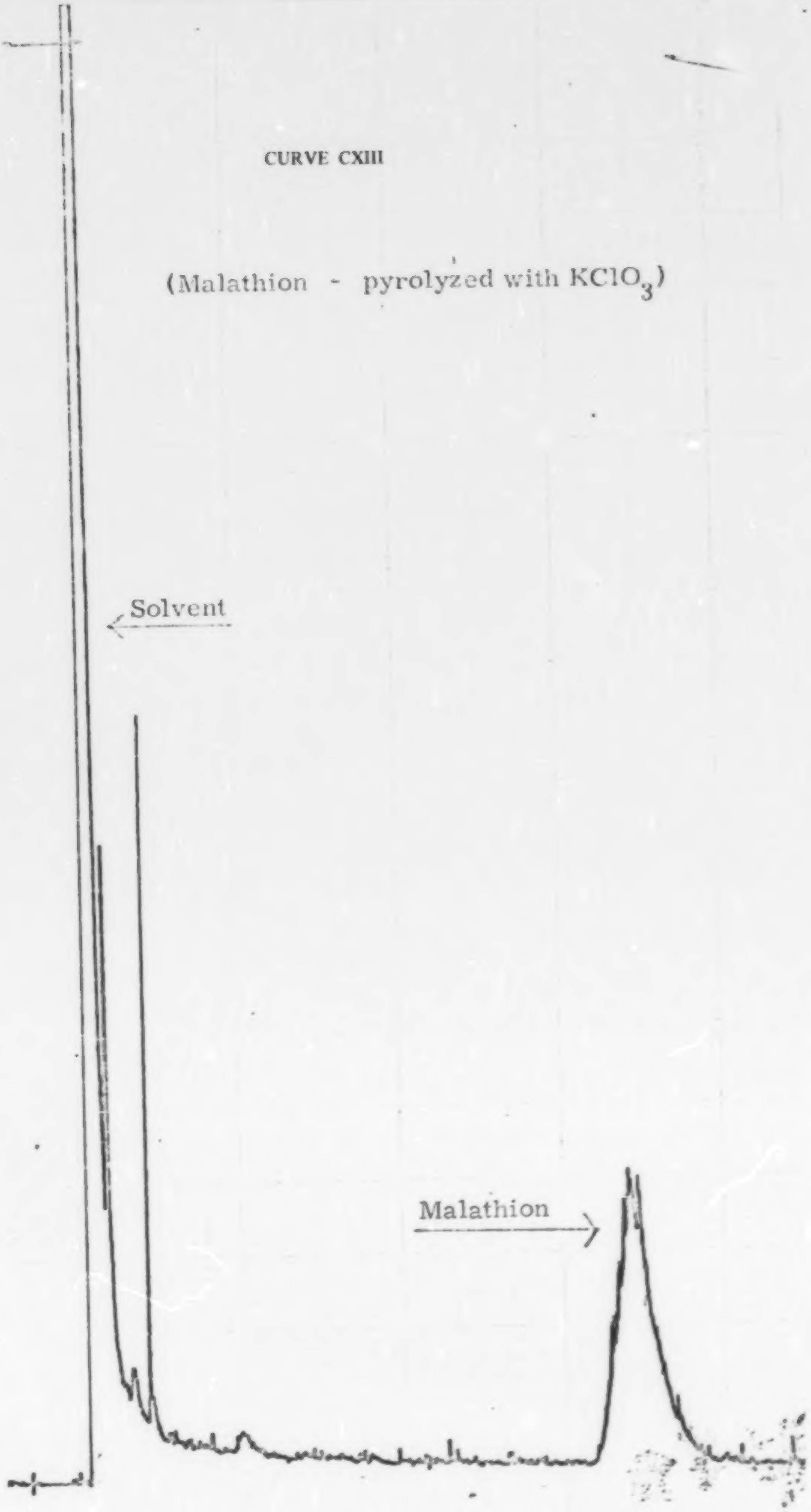
CURVE CXII



(Malathion - pyrolyzed with mineral oil)

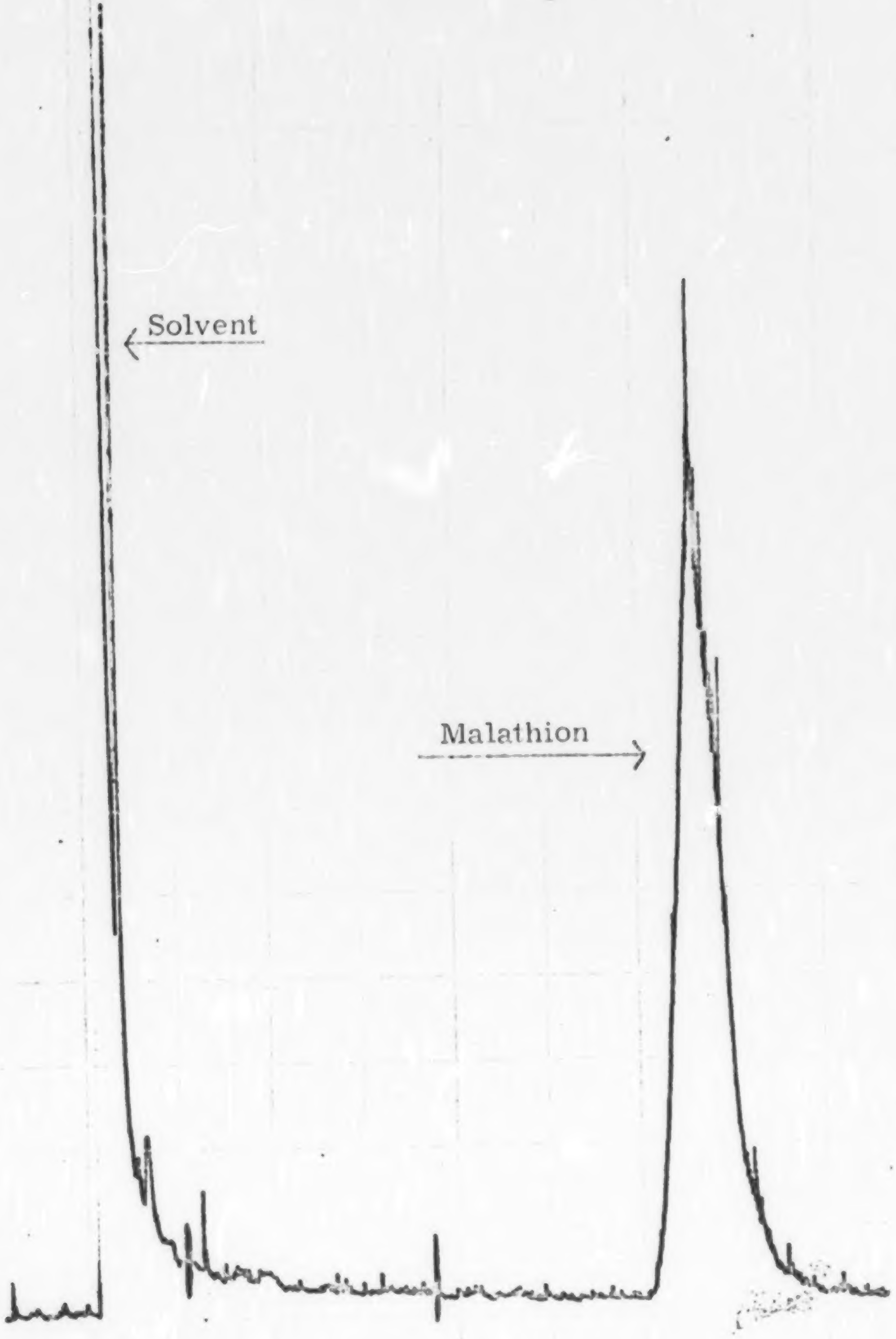
CURVE CXIII

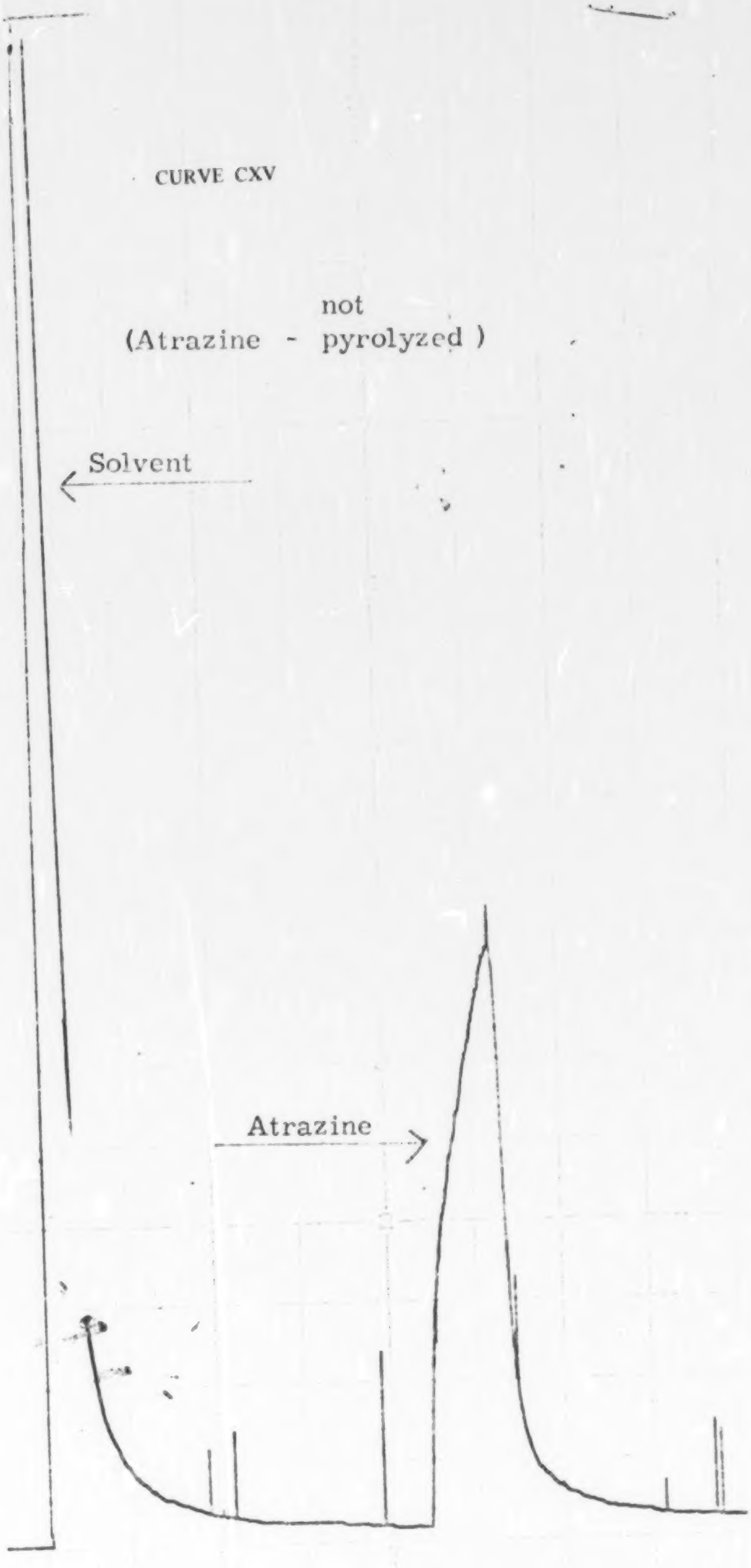
(Malathion - pyrolyzed with $KClO_3$)



CURVE CXIV

(Malathion - pyrolyzed with mineral oil and $KClO_3$)



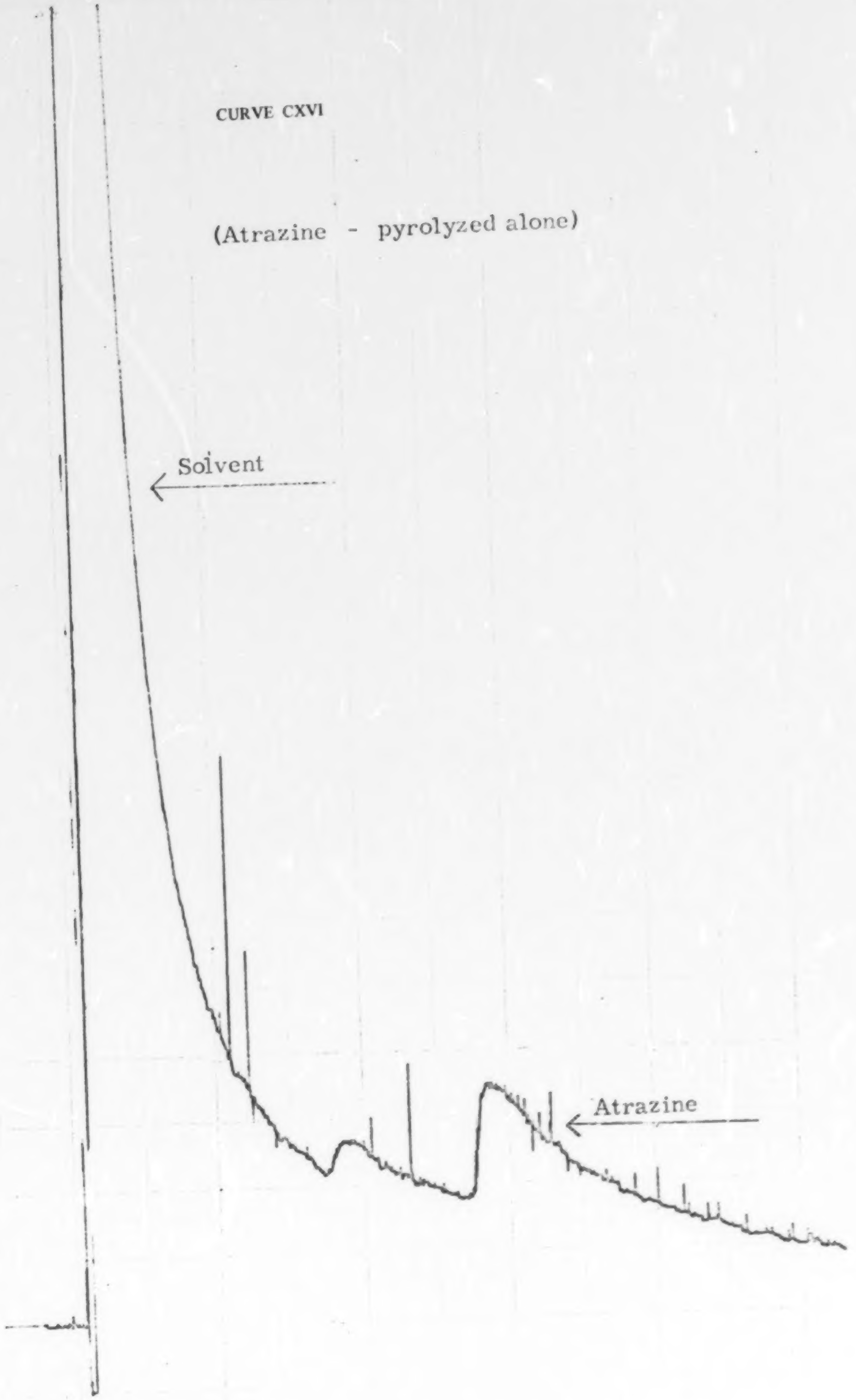


CURVE CXV

not
(Atrazine - pyrolyzed)

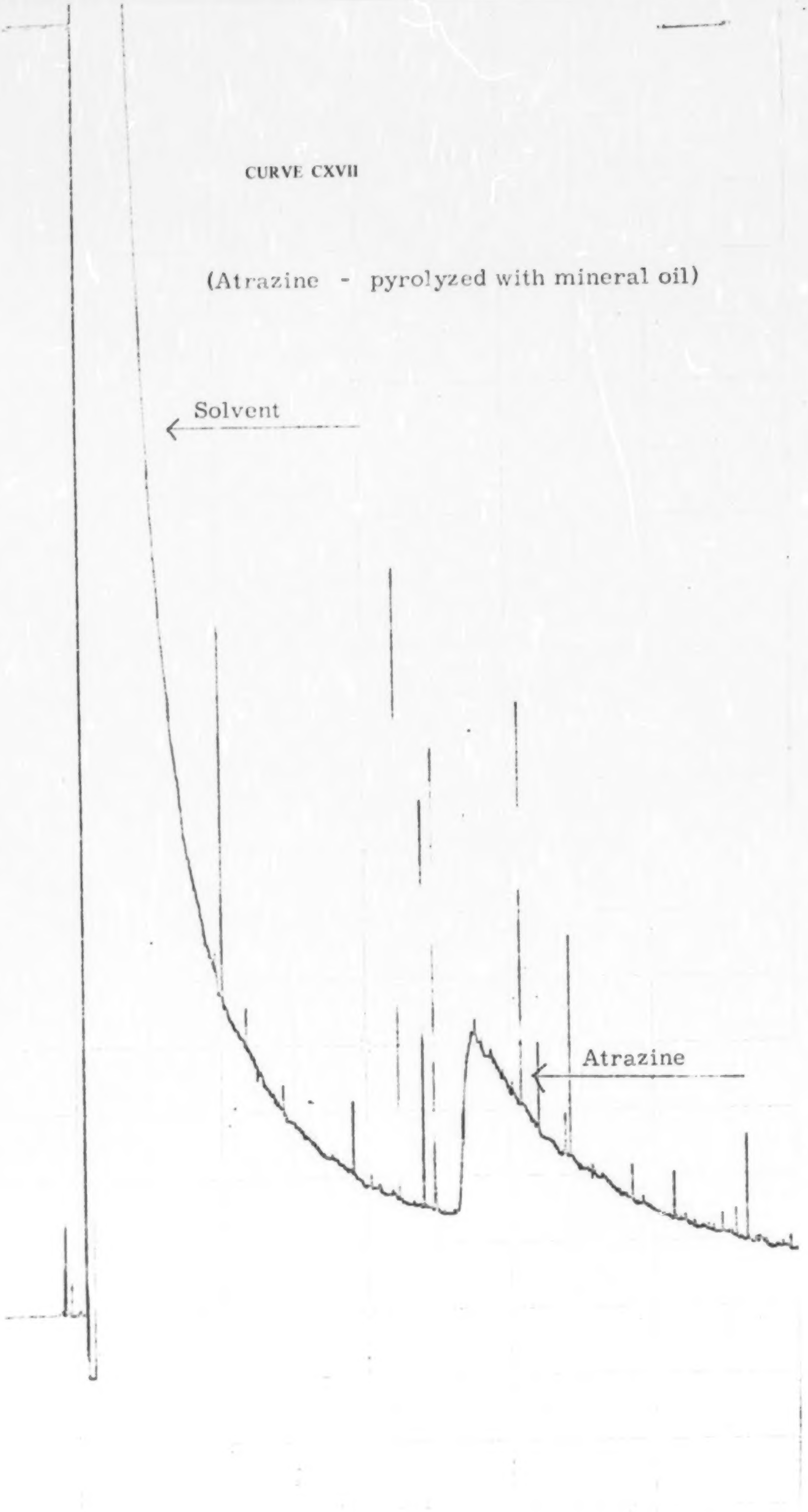
CURVE CXVI

(Atrazine - pyrolyzed alone)



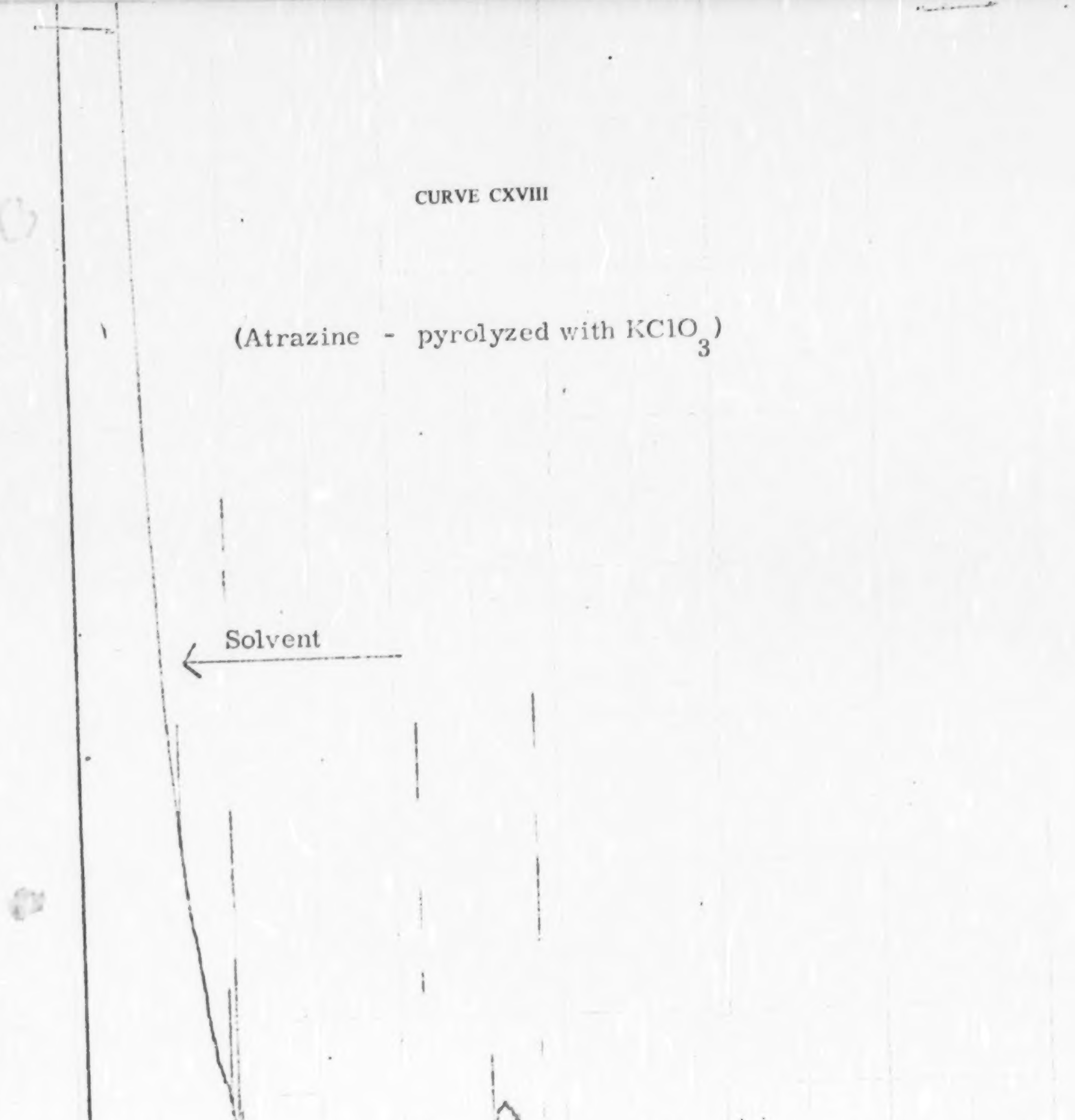
CURVE CXVII

(Atrazine - pyrolyzed with mineral oil)



CURVE CXVIII

(Atrazine - pyrolyzed with $KClO_3$)



CURVE CXIX

(Atrazine - pyrolyzed with mineral oil and $KClO_3$)